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The influence of cold work on the wettability of Pb-FREE solders on copper

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THE INFLUENCE OF COLD WORK ON THE WETTABILITY OF Pb-FREE SOLDERS ON COPPER

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ABSTRACT

THE INFLUENCE OF COLD WORK ON THE WETTABILITY OF Pb-FREE SOLDERS ON COPPER

by Paul B. Fojas

The effect of cold work on the wettability of copper substrates by Sn-3.5Ag, Sn-37Pb, Sn-9Zn, and Sn-0.7Cu solders was investigated using a wetting force balance. Copper substrates were cold worked between 0% and 50% reduction in thickness and the wetting force measured at 245°C and T_m + 62°C. In general, the wetting force was found to be directly related to the extent of cold work. The other factors found to affect wetting force were the solder bath temperature and the type of flux, either aqueous or no-clean, used. The wetting forces were found to be higher at the solder bath temperature of T_m + 62°C as compared to 245°C. Use of an aqueous flux resulted in higher wetting forces, compared to the no-clean flux. The combination of high degree of cold work (greater than 40%), test temperature (T_m + 62°C) and aqueous flux resulted in the highest wetting forces. Of the three lead free solders tested Sn-3.5Ag exhibited the highest wetting force.

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CHAPTER ONE
INTRODUCTION

1.1 Solder and the Electronics Industry

Solder is ubiquitous in the electronics industry where it is the primary means of joining electronic components such as resistors, capacitors, or packaged integrated circuits to printed wiring boards (PWB). Within these components solders perform electrical, thermal, and mechanical functions. For instance, the solder provides an electrical and mechanical conduit between joined parts. Thermally, solder allows for the dissipation of heat generated by components. Due to these important functions the quality and integrity of solder in the joints is critical to the functioning of the electronic components or assembly.

One of the many uses of solder in the electronics industry is in the mounting of a microelectronic device or package to a printed wiring board (PWB). This is commonly referred to as level 2 packaging (as opposed to level 1 packaging which involves bonding of a silicon die to a substrate, followed by encapsulation) [1]. Attachment of the electronic component to the PWB is done by either pin-through-hole (PTH), Figure 1, or surface mount approaches (SMT), Figure 2 [1]. The soldering of the PTH printed wiring board involves wave soldering, where the PTH and PWB are taken through a solder bath and solder joints form by capillary action [1]. Alternatively, SMT printed wiring boards can be processed via reflow soldering where solder paste is applied to the mating surfaces, the parts are mated, passed through an oven and heated to a temperature sufficient to melt the solder. Upon cooling the joint is formed [1].

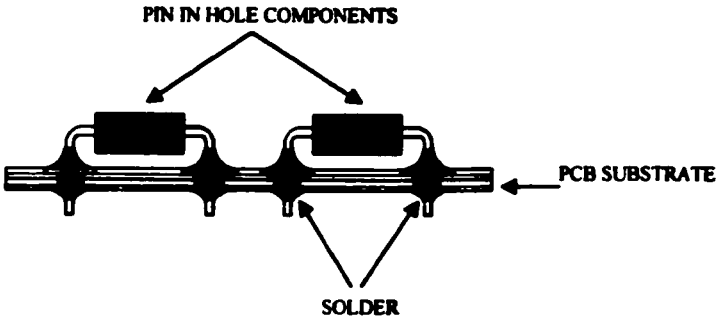

Figure 1: Pin through hole connection of a microelectronic component to a printed wiring board [1].

Figure 2: Surface mount connection of a microelectronic component to a printed wiring board [1].

1.2 Wetting and Cold Work

As can be inferred from the foregoing the quality of the solder is critical in the overall functioning of the electronic assembly. One of the most important solder properties is wettability, which is the ease with which molten solder can coat or wet a surface. Wetting is a surface phenomenon much like catalysis, tribology and wear/friction [2,3]. The surface of a material is a complex and unique region; it has physical properties that can be distinct from the bulk material. In particular, atoms and molecules located at the surface tend to experience significantly different forces from those in the bulk material because of different numbers and types of neighboring atoms and molecules [2]. Additionally, at an interface between a material surface and a liquid an electrical potential across the interface can exist [2,3]. These factors can result in the occurrence of many physical and chemical phenomenon unique to surfaces. For instance, attractive forces on

the surface can cause a concentration and orientation of molecules resulting in chemical reactions that have greater rapidity and specificity than similar reactions occurring in the bulk of the material [2]. Also, at the surface unique states of matter can be formed such as monolayers; these are not found in the bulk [3].

The foregoing highlights some characteristics of surfaces which make surfaces particularly important in catalysis, corrosion, tribology, biological and biomedical chemistry and adhesion [2,3]. Thus, modification of the character of the surface can influence how reactions occur on the surface.

One means of modifying the surface is through the application of stress. In particular, residual stresses can affect the Gibbs Free energy of a material surface and bulk and thereby influence reactions. Residual stresses result from the deformation or cold working of a material. As a material is progressively deformed a portion of the energy used to deform the material is stored within the material in the form of lattice distortions, point defects and dislocations [4]. The remainder of the deformation energy is lost as heat.

The stored energy within a work hardened material is much higher than in a non-work hardened material. In the material there is balance between high residual tensile stresses in the interior of the material and high residual compressive stresses at the surface. The end result of deformation is that the material has a higher overall Gibbs Free energy. In the particular case of the material's surface, residual compressive stresses cause an increase in the surface free energy. With the higher surface free energy there is a greater driving force for reactions to occur on the surface of a work hardened material [3-5].

1.3 Lead Frames

One of the most important parts of an electronic component is the lead frame which supports the chip during assembly. Along with solder the lead frame provides the electrical connectivity between the silicon die and the PWB either through PTH or SMT technology, as described in Section 1.1 [1,6]. The typical package assembly involves attachment of the silicon die to the lead frame with an epoxy adhesive. This is followed by wire or tape bonding of the active surface of the die to the inner lead tips of the lead frame. Next, the die and lead frame are encapsulated in a ceramic or glass package. Figure 3 is a schematic illustration of the bonding of a silicon die onto a lead frame, followed by transfer molding of the lead frame and die. The outer leads of the lead frame are then bent and plated with nickel, tin, gold or silver to aid in soldering and increase the shelf life of the electronic component [6].

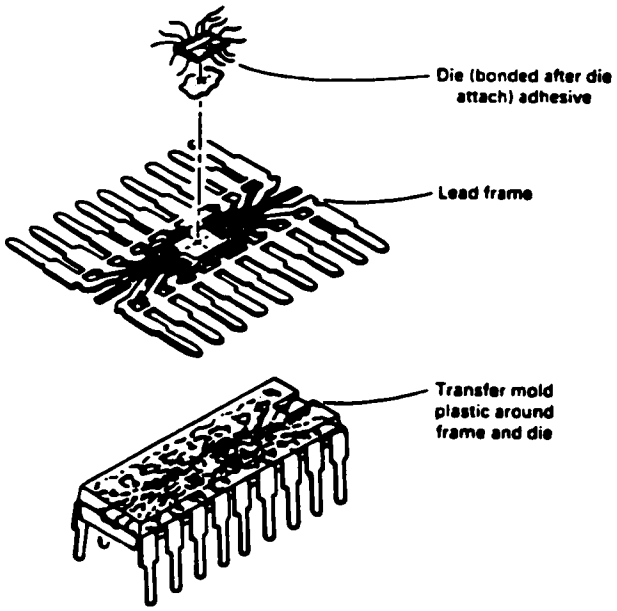

Figure 3: Schematic illustration of die attach followed by transfer molding [6].

The fabrication of lead frames first involves producing lead frame strip from cast ingots of copper alloy, iron nickel (Fe-Ni) or iron nickel cobalt (Fe-Ni-Co). In the case of copper alloys the ingot is hot rolled to a thickness of 12.5 mm and then cold rolled to the final gage before being slit to the required width. For iron nickel and iron nickel cobalt lead frames the ingots are first hot forged prior to hot rolling, cold rolling and slitting. All of the alloys are heat treated at various intervals in the cold rolling process, and after slitting, to reduce residual stresses induced during cold working.

Once the lead frame strip is made it is either stamped or etched and then plated [6]. For purposes of simplicity only the more common stamping technique will be discussed. Fe-Ni, Fe-Ni-Co or copper strip (0.1-0.25 mm thick by 25mm – 100 mm wide) mounted on a reel is fed through a die in a high speed precision press. This die (approximately 300 to 700 mm long) is made of tungsten carbide and consists of about 40 to 200 individual punches. With each stroke of the press the strip advances through the die where it is progressively pierced until the final pattern of the lead frame is obtained. The punched strip is then re-spooled onto a reel. The lead frames are then plated with Sn, Ni, Au or Ag to provide a good surface for soldering. Finally, the plated lead frame strip is sectioned into lengths of six to ten units (175 to 225 mm long) [6].

The cold working and slitting used in producing the lead frame strip, the stamping operation used in the fabrication of the lead frames, and the subsequent bending of the outer leads after packaging all introduce cold work to the lead frame. As discussed previously in Section 1.2, cold work changes the surface energy of a material, with the result that it changes the rate at which reactions can occur on the surface. One such surface reaction is the wetting of solder on the outer lead of a lead frame on an electronic

component. Leads that have been cold worked to a greater extent have a higher surface energy and would be expected to have better wetting properties than leads cold worked to a lesser degree.

This phenomenon is of interest to the microelectronics assembly industry. For example, solders which are impractical because of marginal wetting properties may be rendered usable with the proper cold working of a lead. Moreover, the wetting properties of already useful solders could be improved by judicious cold working of the lead. This could result in a decrease in process time and increase in throughput, which in turn equates to increased productivity. Also, since solderability and wettability related problems result in greater than 70% of solder joint failures, controlling the amount of cold work could result in better wetting and thereby more consistent solder joints and a decreased failure rate [7].

1.4 Lead Based Solders and the Regulatory Environment

Various adverse health effects have been attributed to exposure to lead. These include retarded neurological and reproductive functions and cognitive and behavioral changes [8]. Lead in the form of Pb-Sn solders is widely used in the electronics industry and there is presently a growing effort to restrict the use of lead. Domestically, since the early 1990's numerous legislation has been proposed to restrict or tax lead usage. Three of the more prominent bills were the Reid Bill which proposed reporting and control of lead usage, and the Bradley and Cardin Bills which both proposed taxes on lead and lead containing products [9,10]. Since these bills were first introduced none has gathered enough support to be presented to either the U.S House of Representatives or the U.S.

Senate for a vote. However, over the years there has been growing support for this type of legislation.

Internationally, Europe has mandated through The Directive on Waste From Electrical and Electronic Equipment the discontinuation of the use of lead, mercury, cadmium, hexavalent chromium, and halogenated flame retardants by domestic and foreign manufacturers by January 1, 2004 [11]. Similarly, in Japan there was proposed legislation to prohibit lead in landfills and waste disposal sites. Thus, there is an impetus both domestically and internationally to restrict lead usage. It is likely that more legislation will be proposed and eventually enacted sometime in the future. Therefore, it is imperative that viable alternatives to Pb-Sn solders be developed to meet the increasingly stringent regulatory environment.

The widespread use of leaded solders is attributable to their excellent wetting properties. In general, lead free solders, such as Sn-3.5Ag, Sn-9Zn, and Sn-0.7Cu, have wetting properties that are lower than that of a leaded solder, such as Sn-37Pb. As discussed in Section 1.3 cold working is a possible means of improving the wettability of lead free solders and thereby their viability as a replacement to lead based solders.

The purpose of this research was to determine the effect of cold working on the wettability of copper by selected lead-free solders. In the succeeding chapters wetting theories, the experimental work conducted and the results are presented. Specifically, in Chapter Two the existing wetting theories are reviewed. This is followed by Chapter Three in which the research objectives and hypothesis are discussed. Next, in Chapter Four the experimental methodology utilized in this investigation is described. Then, in

Chapter Five the results and discussion are presented. Lastly, in Chapter Six the conclusion of the investigation is presented, followed by recommendations for areas of future work.

CHAPTER TWO
REVIEW OF EXISTING THEORIES

In this chapter the existing literature on wetting is reviewed. In the first section, the wetting of liquids on solids and the various types of wetting are defined. This is followed by a review of the theories affecting the extent of wetting. Next, the effect of cold work on the extent of wetting of metal substrates by solder is reviewed. The final section is a summary of the various theories of wetting.

2.1 Wetting of Liquids on Solids

A drop of liquid on a solid surface either spreads across the surface forming an almost uniform thin film or spreads to a lesser degree and stays as a discrete drop [12]. The extent to which the liquid spreads, as measured by the contact angle θ, the angle the drop makes with the solid, is a quantitative measure of the extent of wetting or wettability of the surface by the liquid [12]. When $\theta = 0°$ complete wetting is said to occur. A contact angle of $0° < \theta < 90°$ corresponds to a condition of incomplete or partial wetting. A contact angle of $\theta \geq 90°$ is indicative of non-wetting [1,9]. This is shown in Figure 4.

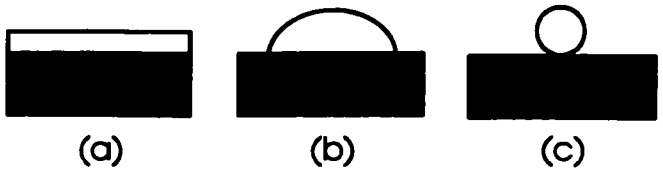

Figure 4: Wetting types: (a) complete wetting, (b) partial wetting and (c) non-wetting [12].

The two typical methods of evaluating the extent of wetting are the sessile drop method and the wetting force balance. The sessile drop method involves placing a drop of the liquid to be tested on a substrate. The drop is observed from the side and the contact

angle is manually read from a goniometer scale in the eyepiece of a microscope. Alternatively, a video camera and computer can be used to automatically measure the contact angle. A schematic of a typical sessile drop measurement apparatus is shown in Figure 5.

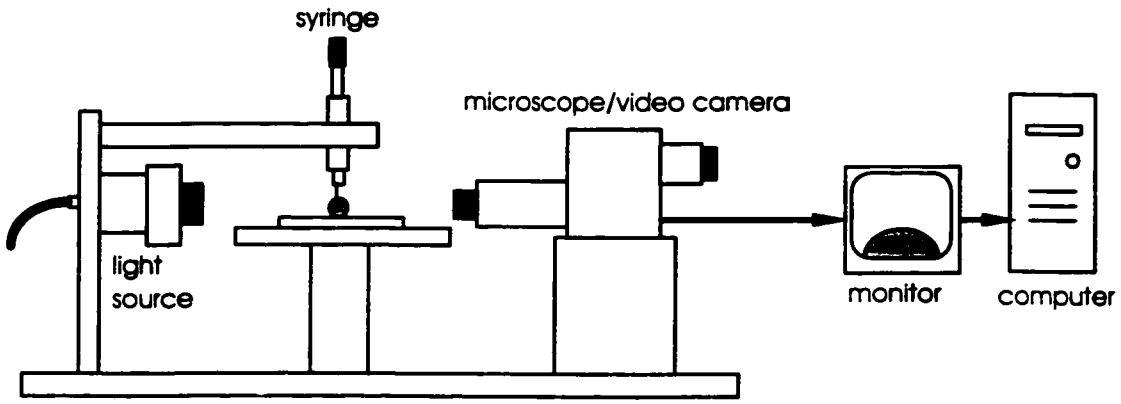

Figure 5: Sessile drop measurement apparatus.

The alternate method of assessing wetting is through the use of a wetting force balance, schematically shown in Figure 6. This instrument measures the force of interaction between a molten alloy and substrate as the substrate is immersed and then extracted from the molten alloy. In the operation of a wetting force balance, the specimen is suspended from a sensitive balance and immersed edgewise, at a predetermined and controlled rate, and to a specified depth, into the molten solder. As a result of the interaction between the molten solder and the specimen the wetted coupon is subject to time variant vertically upward buoyancy forces and downward surface tension forces shown in Equations 1a and 1b.

$$F = \text{wetting force} - \text{buoyancy forces} \qquad \text{Equation 1a}$$

This can be expressed alternatively as:

$$F = \gamma p \cos\theta - \rho g v \qquad \text{Equation 1b}$$

Where:

F = net force acting on the specimen
γ = surface tension of the molten solder under the flux
p = specimen perimeter
g = acceleration due to gravity
ρ = molten solder density
v = immersed specimen volume
θ = contact angle

The forces on the sample are detected by a transducer and are converted into an electrical signal, which is in turn recorded by the data acquisition system in a computer. Higher wetting forces are indicative of smaller wetting angles and therefore better wetting.

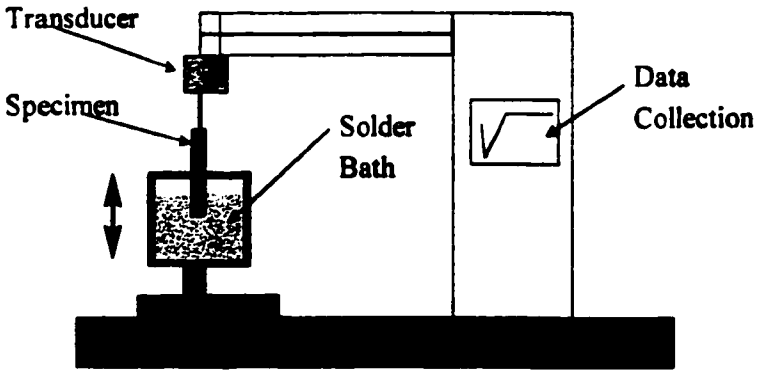

Figure 6: Schematic of a wetting force balance [4].

Researchers have extensively investigated the wetting of liquids on solids. In 1805, Young observed that a drop of liquid resting on a substrate is a three phase system consisting of a (1) liquid on a (2) solid surrounded by a (3) gas in which there is a balance

between competing surface forces from the three phases [5]. At equilibrium the drop forms a contact angle θ with the solid surface which is expressed by Equation 2:

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl} \cos \theta \qquad \text{Equation 2}$$

where γ_{gs} is the surface tension of the solid in the particular environment, γ_{ls} is the interfacial energy between the solid and the liquid and γ_{gl} is the surface tension of the liquid in the environment [1,13]. This is depicted in Figure 7. This equation is known as the Young equation. It was based on a mechanical analysis of the resultant forces at the three-phase contact line.

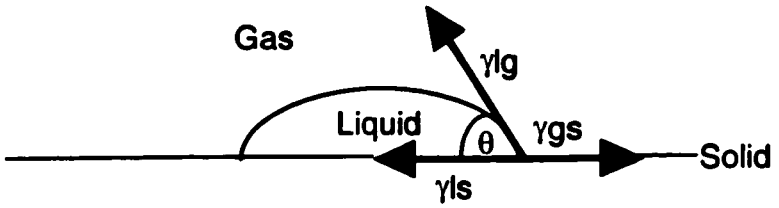

Figure 7: The contact angle θ formed by a liquid drop on a solid surface and the three tangential forces acting in equilibrium.

Thermodynamically, the Young equation shows that good wetting occurs when there is a net lowering of the total surface free energy. In other words, the surface energy of the solder is lowered by the formation of an interface that is at a lower surface interfacial energy [1].

2.2 Factors Affecting the Extent of Wetting

Since Young's initial work extensive research has been done to determine the factors that affect the extent of wetting. There are presently two prevailing theories concerning the factors by which the flow of liquid metals on solid surfaces is controlled: surface

roughness and solubility [13,14]. Wenzel [15] was one of the first to investigate the effect of surface roughness on wetting. He showed intuitively that surface roughness increased surface area and would result in enhanced wetting. This is shown in Equation 3:

$$R = \cos \theta_r / \cos \theta_o \qquad \text{Equation 3}$$

where R is the surface roughness factor (the ratio of the apparent and true surface areas of the solid), θ_r is the apparent contact angle and θ_o is the true contact angle. The apparent contact angle, θ_r, is the angle between the liquid and the apparent solid surface or top of the surface asperities due to roughness. The true contact angle, θ_o, is the angle between the liquid and the surface at the air/liquid/solid contact boundary. The apparent and true contact angles are depicted in Figure 8.

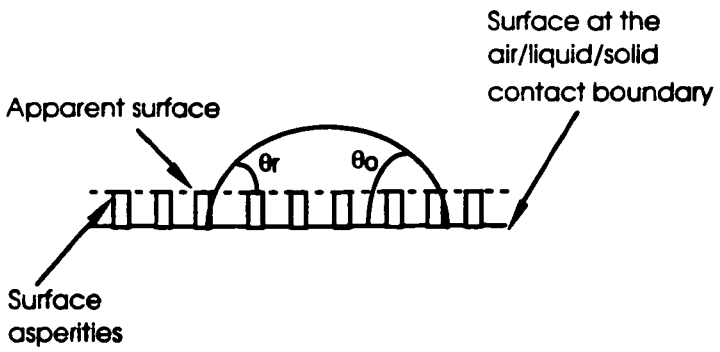

Figure 8: Depiction of the apparent and true contact angles of a liquid on a rough surface.

The difference between the true contact angle and apparent contact angle comes about due to irregularities on the solid surface due to surface roughness. Wenzel reasoned that roughening a smooth surface increases its surface area and therefore the intensity of the surface free energy. Thus, a smooth solid that wets will wet better if it is roughened.

Conversely, a smooth solid that wets poorly will wet even more poorly when roughened [12,15].

In contrast, Shuttleworth and Bailey [16] derived a relation , shown as Equation 4, which directly contradicts the above Wenzel relation:

$$\theta_r = \theta_o \pm \alpha \qquad \text{Equation 4}$$

where θ_r is the true contact angle, θ_o is the apparent contact angle and α is the maximum angle of the local surface. This expression predicts that the apparent contact angle would increase as surface roughness increases. Nicholas and Crispin [17] eventually resolved the discrepancy between the Wenzel and Shuttleworth and Bailey relations by showing that Wenzel wetting is prevalent in well wetting systems such as liquid copper on mild steel or on stainless steel. On a moderately wetting system such as liquid tin on copper or poorly wetting systems such as copper on aluminum wetting was impeded, as predicted by Shuttleworth and Bailey. It was explained that the surface asperities formed by surface roughening formed a type of potential energy barrier that only the most energetic liquids, as measured by the liquid's enthalpy, can overcome. The research results correlated enthalpies of liquids with wetting but there were inconsistencies with some of the data and thus this explanation was not conclusively proven [17].

One of the most significant findings concerning wetting was by Bailey and Watkins [18] in 1951. They showed that alloying or the formation of intermetallic compounds between the liquid metal and the metal substrate was a necessary condition for wetting. These

investigators tested 38 pairs of liquid metal and substrate (solid metal) combinations consisting of the following:

Liquid metal: Ag, Sb, Te, Zn, Pb, Cd, Bi, Sn, Al

Substrate: Fe, Ni, Cu, Au, Ag

and determined that in instances where an intermetallic compound was expected to be formed at the interface between the solid and liquid at the given test conditions wetting occurred. Similarly, in test conditions where solid solutions were expected wetting occurred. Conversely, if no compounds or solid solutions were expected at the given test conditions de-wetting or non-wetting occurred. Adamec and Rhoda [19] went on to substantiate these findings with their work on the wetting of nickel chromium alloys by silver. These authors investigated how additions of palladium or copper to silver increased the wettability of silver on Inconel and Inconel X alloys. Silver is neither soluble nor forms intermetallic compounds with Inconel and Inconel X. Thus, it does not wet these alloys well. It was found that additions of about 10 weight percent palladium or platinum to silver increased the wetting of the silver alloy. The palladium or platinum, which was immiscible in the silver, formed a noble thin film phase on the Inconel alloy surface. This thin film was in turn wet by the silver rich phase. Thus, Adamec and Rhoda showed that wetting could be achieved on two normally non-wetting components by the use of an intermediary component that alloys with the two other components. Wassink [20], reviewed the findings of the above two investigators and justified their results based on thermodynamics. He argued that greater metal solubility is related to a lowering of the interfacial energy when these metals are brought into contact with each

other. Thus, based on the Young, equation the reduction in interfacial energy will result in wetting.

The work reviewed in the foregoing was the foundation for understanding the phenomenon of wetting. In Section 2.3 a more recent factor that has been found to influence wetting behavior, cold work, is reviewed.

2.3 Effect of Cold Work and Wetting

One of the factors that has not been extensively investigated is the effect of residual surface stresses on wettability. Residual stresses, in particular those resulting from cold working a material, increase the extent of wetting. The strain energy used in the plastic deformation during cold working is stored within the material as dislocations and other imperfections such as point defects. Thus, a strain hardened metal has a higher internal energy than an unstrained one. Moreover, the surface of the metal also has a higher surface free energy as a result of the strain hardening. From the Young equation:

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl} \cos \theta \qquad \text{Equation 2}$$

it can be noted that γ_{gs} reaches a maximum when the contact angle θ approaches 0° ($\cos \theta = 1$) and a minimum when θ approaches 90°. Thus, a higher surface free energy results in better wetting. Thermodynamically, the shape of the drop on the substrate and resultant contact angle that forms is a function of the Gibbs free energy of the system. Since a thermodynamic system is always tending towards a net lowering of the Gibbs free energy, a liquid drop on a substrate will take a shape so as to minimize the Gibbs free energy of the system. In a system composed of a liquid drop on a substrate, cold working the

substrate results in an increase in stored energy and the Gibbs free energy of the substrate, and therefore the system as a whole. To achieve thermodynamic stability in this system the contact angle of the liquid drop has to decrease in order to minimize the Gibbs free energy of the system.

Osawa et al [21] was one of the first to observe the influence of cold work on the extent of wetting. Copper and low carbon steel substrates were cold rolled to a thickness of 0.3 mm, which represented a 90 percent reduction in thickness for the copper substrates and a 75 reduction in thickness of the steel substrates. Next, the substrates were annealed at temperatures ranging from 373K to 1073K, following which the wetting of eutectic Sn-37Pb solder was measured in terms of spreading area. It was found that the as rolled samples which had the highest amount of cold work, exhibited the greatest wetting and then wetting decreased, reaching a minimum, as the recrystallization temperature of the respective metals was reached. At the recrystallization temperature new grains were nucleated and began growing. As the annealing temperature increased beyond the recrystallization temperature to the secondary recrystallization temperature wetting began increasing again. Secondary crystallization is a phenomenon that occurs in fine-grained recrystallized metals in which some grains grow rapidly at the expense of other grains. The driving force for secondary recrystallization is the decrease in surface energy, whereas in recrystallization the driving force is a decrease in stored energy [22]. The results of Osawa's tests are shown in Figures 9 and 10.

Osawa speculated that the changes in surface free energy that caused the observed changes in wetting behavior resulted from a re-orientation of the primary crystallographic

plane from a high energy plane to a low energy plane. In the particular case of the copper substrates it was postulated that a re-orientation of the FCC crystal occurred from (110)

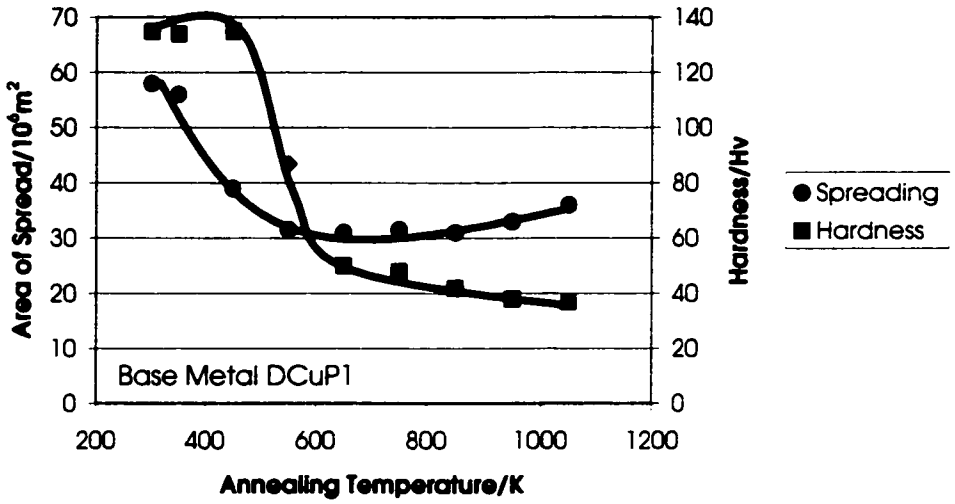

Figure 9: Effect of annealing temperature on hardness and spreading area of solder on cold rolled copper [21].

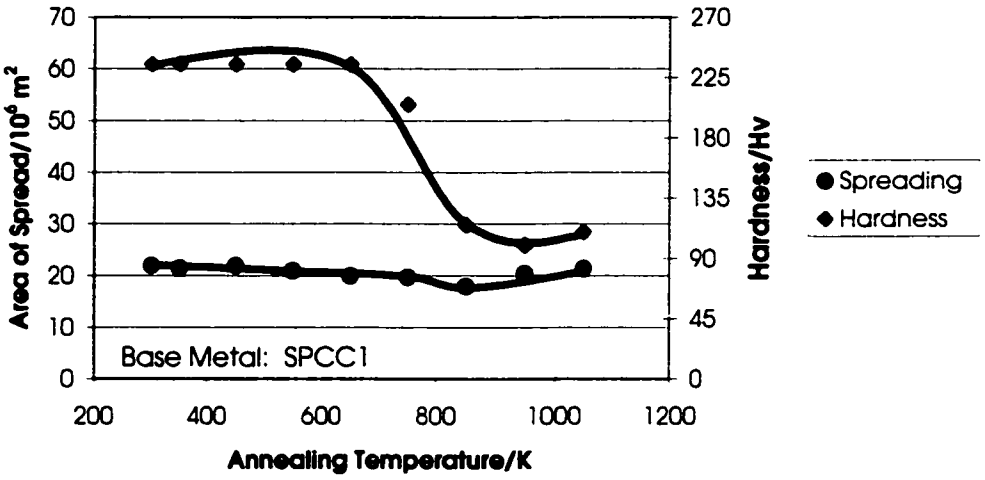

Figure 10: Effect of annealing temperature on hardness and spreading area of solder on cold rolled mild steel [21].

to (100). At secondary recrystallization another re-orientation occurred from the low energy plane back to a higher energy plane. Osawa's conclusion is highly plausible but his data showed no definitive evidence, such as x-diffraction scans, to validate that re-orientation of the crystal had occurred.

In a similar study, Hasouna et al. [13] investigated the effects of cold working on the wettability of solid copper by liquid tin. Copper sheet was cold worked between 6 and 31 percent reduction in area by rolling or pressing. Liquid tin was then applied to the sample surface in a H_2 atmosphere and the resulting contact angle between the sample and the drop of tin was measured using the sessile drop method. It was found that the contact angle decreased as cold work increased as shown in Table I. Based on the Young equation it was concluded that the surface free energy of the material increased due to the cold working. Similar to Osawa, Hasouna related this change in surface free energy to a change in the primary crystal orientation of the sample surface.

Table I: Effect of Cold Working on Contact Angle between Cu and liquid Sn [13].

Reduction of Thickness (%)	Contact Angle
0	42°
6	33°
13	29°
18	22°

Hasouna's finding are similar to those reported by Osawa. However, there were inconsistencies in both his methodology and experimental procedure. First, it seems from the reported data that only one sample per test condition was evaluated. Thus, the reported results lack statistical validity because the experimental error could not be determined. Secondly, the range of cold work conditions was too narrow to effectively track the effect of cold work on contact angle. More tests should have been performed beyond 31 percent reduction of thickness in order to more clearly quantify the effect of cold work on contact angle. Thirdly, a correlation between (111) peak intensity and contact angle was stated but the expected correlation between cold working process, percent reduction of thickness and contact angle was not proven. For example it would be expected that since rolling decreases (111) peak intensity more than pressing that the rolled samples should exhibit better wetting than the pressed samples. Yet, the results showed little difference between pressed and rolled samples that were cold worked the same amount. Lastly, no XRD was performed on the cold worked samples to quantify the change in (111) peak intensity. He merely extrapolated his findings, from conducting XRD on mechanically polished, electrochemically polished and annealed samples, to the cold worked samples without experimental evidence. Thus, Hasouna's conclusions are somewhat inconclusive.

Collazo also investigated the effect of varying cold work on the wetting of copper by solder [4]. His study included two different solders (63Sn-37Pb solder and a 77.2Sn-20In-2.8Ag) to determine how different solder types wet in relation to cold work. In this investigation copper sheet was cold worked from 10 to 50 percent reduction in thickness and then tested using a wetting force balance. The results are shown in Figure 11.

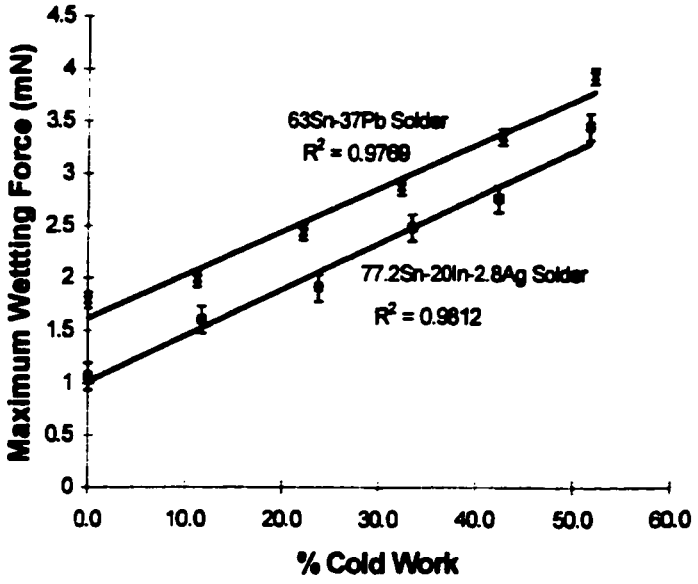

Figure 11: Maximum wetting force as a function of cold work for 77.2Sn-20In-2.8Ag solder and 63Sn-37Pb solder [4].

Collazo observed that progressive cold working resulted in a linear increase in wetting force for both solder types tested. However, the wetting force of the 63Sn-37Pb solder for all degrees of cold work was shifted about 0.6-0.7 mN higher than similarly cold worked samples tested in 77.2Sn-20In-2.8Ag solder. This shows that 63Sn-37Pb solder wets copper better than 77.2Sn-20In-2.8Ag solder. Similar to Osawa, he concluded that the strain energy expended during cold working was stored as dislocations within the material which then increased the surface free energy of the material. Consequently, this caused an increase in the maximum wetting force [4].

Collazo was more thorough in his experimentation than Hasouna. He determined his experimental error by testing five samples per experimental condition. Therefore, his results have statistically validity. Next, his testing was conducted at a greater range of cold work, from 10 to 50 percent reduction in thickness. Thus, the expected trend of

increased wettability with cold work noted by Hasouna is more clearly delineated in Collazo's experimental results.

2.4 Summary

Young was the first to characterize the phenomenon of wetting with the Young equation. Wenzel showed that surface roughness influenced wetting behavior. Nicholas and Crispin followed up Wenzel's initial work and showed experimentally that his findings were valid for well wetting systems and for moderate and poorly wetting systems the relation derived by Shuttleworth and Bailey was more appropriate. In 1951 Bailey and Watkins reported that alloying or the formation of intermetallic compounds was necessary for wetting to occur. Adamec and Rhoda went on to show that in systems where alloying did not occur the addition of a third component which alloyed with the other two resulted in wetting. Lastly, Osawa, Hasouna and Collazo clearly showed that stored surface energies derived from cold work resulted in an increase in the extent of wetting. Therefore, the purpose of the present investigation was to add to the body of knowledge already contributed by the above investigators, specifically, to determine how stored surface energy from cold working affects the wetting behavior of different solder and flux combinations on copper.

CHAPTER THREE
RESEARCH OBJECTIVES AND HYPOTHESIS

The cold working of a metal results in the creation of dislocations within the metal. These dislocations combine and result in an increase in the free energy of the material. This free energy has a surface component known as the surface free energy. A change in the surface free energy of a material results in a change in the reactions that can occur on the surface.

The wettability of a material is dependent upon surface free energies as shown in the Young equation:

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl} \cos \theta \qquad \text{Equation 2}$$

It is therefore expected that the stored surface energy derived from cold working a material will influence its wettability characteristics. Moreover, progressive cold working will increase wettability.

The objective of this study was to investigate the effect of progressive cold working on the wettability of Sn-3.5Ag, Sn-37Pb, Sn-9Zn, and Sn-0.7Cu solders, using aqueous and no-clean fluxes, on copper substrates at 245°C and T_m + 62°C, where T_m is the liquidus temperature of the solder alloy. The independent variables investigated were solder type, flux type, test temperature, amount of cold work. The dependent variable to be investigated was the maximum wetting force.

CHAPTER FOUR
EXPERIMENTAL METHODOLOGY

The experimental work performed was divided into three major categories, sample preparation, testing, and analysis. The experimental procedure is summarized in Figure 12.

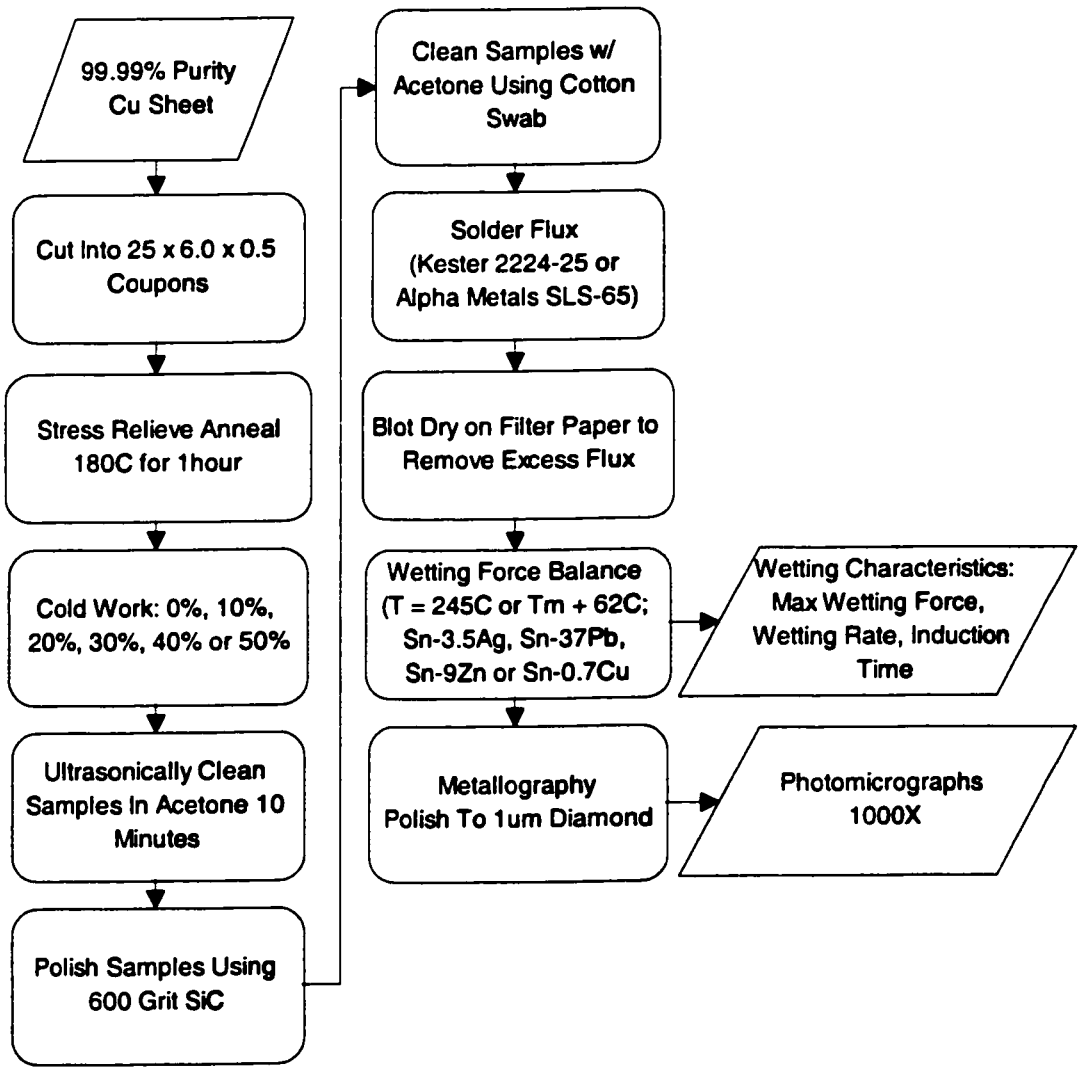

Figure 12: Experimental procedure

4.1 Sample Preparation

Copper sheets with a thickness of 0.5 mm and a purity of 99.99% were purchased from Goodfellow Corporation. These sheets were first sheared, and then milled to yield 6.0 ± 0.25 mm wide x 25.0 ± 1 mm long coupons. These coupons were then stress relief annealed in a furnace at a temperature of 180°C, which is the stress relief temperature of copper, for 1 hour. Next, the samples were removed from the furnace and allowed to air cool.

The cold working of the samples consisted of rolling the samples, to 10, 20, 30, 40, and 50 percent reduction in thickness using a Stanat Rolling Mill. The rolling was done in 10 percent increments such that during each pass through the rolling mill the sample's thickness was incrementally reduced by 10 percent. After each pass the thickness of the samples was measured using a Mitsutoyo dial caliper. The percentage of cold work was calculated according to Equation 5:

$$\% CW = (A_i - A_f)/A_i \qquad \text{Equation 5}$$

Where:

$\% CW$ = percent cold work
A_i = initial area (length x width)
A_f = final area (length x width)

Subsequent to cold working the samples were ultrasonically cleaned in acetone for 10 minutes and dried. All samples were then polished on 600 grit SiC paper. Polishing of all samples using 600 grit SiC paper was done to give them a comparable surface roughness. As discussed in Section 2.2, in particular the work of Wenzel [15], the surface roughness of a material can greatly affect its wetting properties. Thus, the

samples for this investigation were polished to a consistent surface roughness to minimize the influence of surface roughness on the wetting force tests.

4.2 Testing

The combinations of solders, fluxes, solder bath temperatures and extent of cold work employed in this study are summarized in Table II.

Table II: Experimental Matrix

		Solder Bath Temperature											
		245°C						T_m + 62°C					
Flux	Solder	% Cold Work											
		0	10	20	30	40	50	0	10	20	30	40	50
Aqueous	Sn-3.5Ag	X	X	X	X	X	X	X	X	X	X	X	X
	Sn-37Pb	X	X	X	X	X	X	-	-	-	-	-	-
	Sn-9Zn	X	X	X	X	X	X	X	X	X	X	X	X
	Sn-0.7Cu	X	X	X	X	X	X	X	X	X	X	X	X
No Clean	Sn-3.5Ag	X	X	X	X	X	X	X	X	X	X	X	X
	Sn-37Pb	X	X	X	X	X	X	-	-	-	-	-	-
	Sn-9Zn	X	X	X	X	X	X	X	X	X	X	X	X
	Sn-0.7Cu	X	X	X	X	X	X	X	X	X	X	X	X

Notes:
1. Testing on Sn-37Pb was not performed at T_m + 62°C since T_m for this solder is 189°C and Tm + 62°C equals 245°C.
2. In the above experimental matrix "X" represents five test samples.

The procedures and parameters used for the wetting force balance tests in this investigation were based on IPC-TM-650. Prior to testing all samples were cleaned (degreased) with acetone using a cotton swab. Then, the samples were immersed in solder flux, either aqueous or no clean, to a minimum depth of 10 mm for 30 seconds. Excess flux was drained from the samples by using clean filter paper.

Testing was conducted using a Multicore Solderability Tester, also known as a wetting force balance and Multicore MUSTMATE 110 v2.0 software. A representation of the wetting force balance is shown as Figure 13.

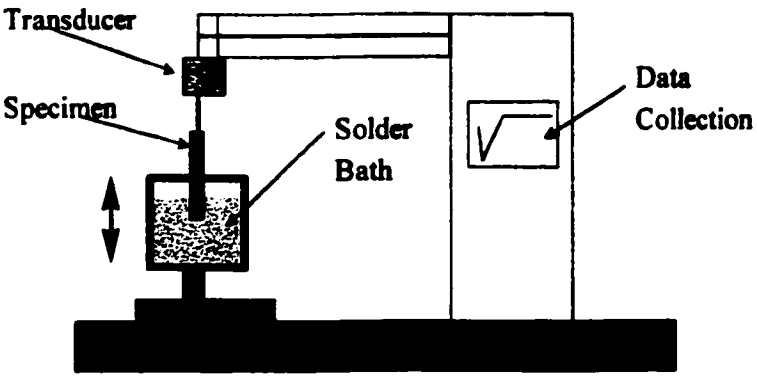

Figure 13: Schematic of a wetting force balance [4].

Using this wetting force balance samples were immersed in a molten solder bath at a temperature of either 245°C or T_m + 62°C and were then drawn out of the bath at a rate of 20-25 mm/sec. The first temperature, 245°C, represents the current surface mount reflow temperature for Sn-37Pb used in industry. T_m + 62°C represents a temperature of 62°C above the liquidus temperature of the particular solder. These measurements were done because the reflow temperature for each alloy would be dependent on its melting temperature. A soldering alloy with a 140°C liquidus temperature could be reflowed at about 180-190°C, which is much lower than the 220-240°C range for eutectic Pb-Sn solders. By measuring the wetting force of the alloys at a constant temperature value above the melting point, it was thought that wetting force on Cu could be more accurately characterized for manufacturing purposes [1].

Four types of solders, Sn-3.5Ag, Sn-37Pb, Sn-9Zn and Sn-0.7Cu, were used in combination with two different types of fluxes, Kester 2224-25 (aqueous) and Alpha Metals SLS-65 (no clean), which are commonly used in the microelectronics assembly industry. Besides the test specimens that were cold worked from 10 to 50 percent, non-cold worked (0% reduction in area) samples were also tested as a reference. Five samples were tested for each combination of extent of cold work, temperature, solder and flux.

The resulting data was a wetting force curve similar to that shown in Figure 14. From the wetting curve the two primary parameters that can be calculated are wetting time (T_w) and maximum wetting force (F_{max}). Wetting time is the time required for the curve to cross the buoyancy corrected zero axis. The maximum wetting force is a measure of the force of interaction between a molten alloy and substrate as the substrate is immersed and then extracted from the molten alloy. More importantly, it is a measure of the wettability of a liquid on a surface and is the maximum wetting force measured relative to the buoyancy corrected zero axis. Thus, by measuring the wetting force of solders on samples that have been cold worked to different extents the effect of cold work on wettability was determined. Large values of maximum wetting force are indicative of a lower contact angle θ and better wetting. The wetting force data in this study were recorded at an accuracy of three decimal places. These data have been rounded off and are reported at an accuracy of two decimal places.

4.3 Analysis

Upon completion of the wetting force balance measurements metallography was performed on the 50% cold work samples at each combination of, solder bath temperature, solder and flux. The metallography involved mounting the entire sample

horizontally in cold mount epoxy followed by progressive grinding on 300 to 600 grit SiC papers. The samples were then final polished on a 1 μm diamond polishing wheel. Photomicrographs were taken of the solder/substrate interface using an optical microscope at a magnification of 1000x.

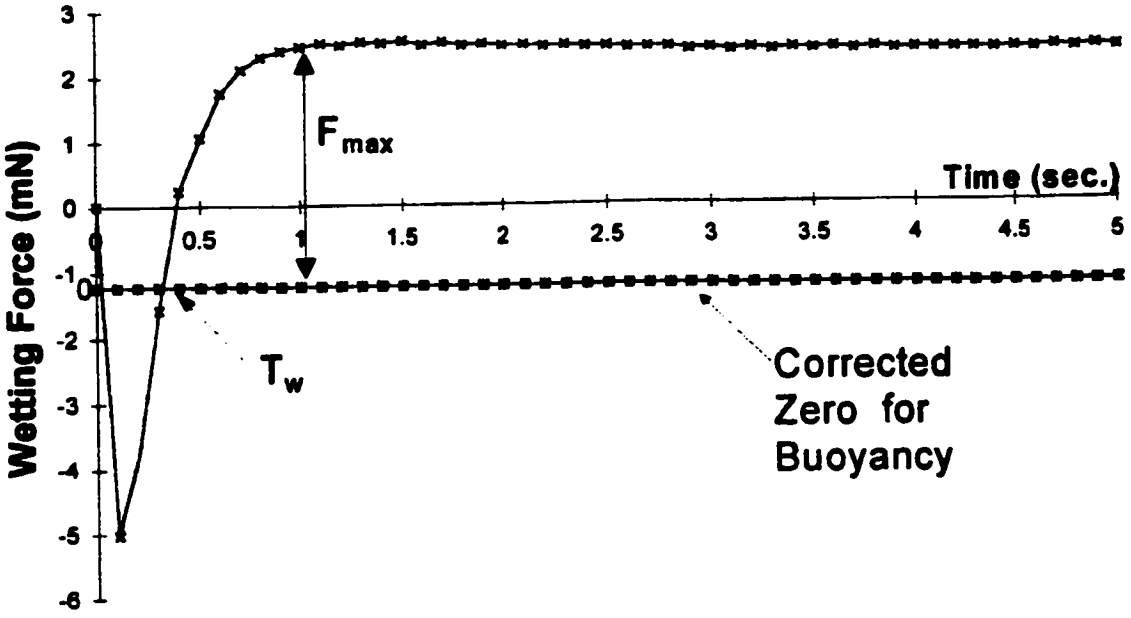

Figure 14: Example of a wetting force curve [4].

CHAPTER FIVE
RESULTS AND DISCUSSION

Overall it was determined that the maximum wetting force increased and the wetting time decreased with the amount of cold working. The maximum wetting force and wetting time were also found to be functions of test temperature and type of flux, either aqueous or no-clean, used. The combination of high extent of cold work (greater than 40%), high solder bath temperature T_m+62 °C and the more aggressive aqueous flux resulted in higher overall maximum wetting forces and lower overall wetting times. The results are summarized in Tables III through VI. Sections 5.1.1 through 5.1.4 contain the detailed wetting results for the specific solders tested. Sections 5.2.1 through 5.2.4 contain the detailed wetting time results. Section 5.3 contains the photomicrographs at the solder/substrate interface of the test samples cold worked to 50 percent reduction in thickness. These photomicrographs show the differences at the solder/substrate interface among the various solder, flux and test temperature combinations investigated.

Table III: Maximum wetting force as a function of cold work results matrix for T=245°C

		% Cold Work					
Solder Flux	Solder	0	10	20	30	40	50
		Maximum Wetting Force (mN)					
Aqueous	Sn-3.5Ag	3.01	3.05	3.46	3.63	4.11	4.30
	Sn-37Pb	3.72	3.85	4.06	4.29	4.58	4.84
	Sn-9Zn	0.46	0.78	0.97	0.93	1.48	1.83
	Sn-0.7Cu	2.85	3.09	2.90	3.40	3.31	3.51
No-clean	Sn-3.5Ag	-4.89	-3.33	-1.58	-0.88	2.40	1.32
	Sn-37Pb	3.41	3.51	3.87	3.65	4.22	3.99
	Sn-9Zn	-5.72	-3.55	-2.68	-2.15	-1.50	-1.20
	Sn-0.7Cu	-4.84	-4.95	-1.95	-2.55	-2.41	-4.18

Table IV: Maximum wetting force as a function of cold work results matrix for $T=T_m+62°C$

			% Cold Work					
			0	10	20	30	40	50
Solder Flux	Solder	Test Temp (°C)	Maximum Wetting Force (mN)					
Aqueous	Sn-3.5Ag	281	3.32	3.67	4.21	3.96	4.09	4.29
	Sn-37Pb	-	-	-	-	-	-	-
	Sn-9Zn	261	0.73	0.95	1.47	1.77	1.75	1.63
	Sn-0.7Cu	289	3.36	3.48	3.68	3.73	3.95	4.01
No-clean	Sn-3.5Ag	281	2.05	2.51	2.04	2.38	3.15	2.26
	Sn-37Pb	-	-	-	-	-	-	-
	Sn-9Zn	261	-3.65	-2.48	-2.14	-2.20	-0.99	-3.01
	Sn-0.7Cu	289	-0.43	0.76	0.89	0.64	1.49	1.00

Notes:
1. Testing on Sn-37Pb was not performed at $T_m+62°C$ since T_m for this solder is 189°C and $T_m+62°C$ is approximately 245°C.
2 T_m denotes the liquidus temperature of solder.

Table V: Time to wetting as a function of cold work results matrix for T=245°C

		% Cold Work					
Solder Flux	Solder	0	10	20	30	40	50
		Time to Wetting (sec)					
Aqueous	Sn-3.5Ag	1.10	0.80	0.70	0.54	0.18	0.19
	Sn-37Pb	0.00	0.00	0.00	0.00	0.00	0.00
	Sn-9Zn	0.49	0.42	0.38	0.29	0.24	0.17
	Sn-0.7Cu	1.28	0.94	0.54	0.51	0.52	0.44
No-clean	Sn-3.5Ag	N/A	0.44	0.77	0.87	0.36	0.60
	Sn-37Pb	0.20	0.27	0.23	0.30	0.25	0.23
	Sn-9Zn	N/A	N/A	N/A	N/A	N/A	N/A
	Sn-0.7Cu	N/A	N/A	N/A	N/A	N/A	N/A

Notes:
1. N/A denotes that sample does not have time to wetting (Tw) value because during testing the wetting force data never intersected the corrected zero for buoyancy line

Table VI: Time to wetting as a function of cold work results matrix for $T=T_m+62°C$

			% Cold Work					
			0	10	20	30	40	50
Solder Flux	Solder	Test Temp (°C)	Time to Wetting (sec)					
Aqueous	Sn-3.5Ag	281	0.30	0.24	0.22	0.16	0.00	0.00
	Sn-37Pb	-	-	-	-	-	-	-
	Sn-9Zn	261	0.32	0.28	0.23	0.18	0.15	0.13
	Sn-0.7Cu	289	0.28	0.23	0.19	0.18	0.16	0.13
No-clean	Sn-3.5Ag	281	0.32	0.39	0.34	0.25	0.18	0.22
	Sn-37Pb	-	-	-	-	-	-	-
	Sn-9Zn	261	N/A	N/A	N/A	N/A	N/A	N/A
	Sn-0.7Cu	289	1.08	0.98	0.57	0.75	0.38	0.94

Notes:
1. Testing on Sn-37Pb was not performed at $T_m+62°C$ since T_m for this solder is 189°C and $T_m+62°C$ is approximately 245°C.
2. T_m denotes the liquidus temperature of solder.
3. N/A denotes that the sample does not have time to wetting (Tw) data because during testing the wetting force data never intersected the corrected zero for buoyancy line.

5.1 Maximum Wetting Force

5.1.1 Sn-3.5Ag

With the Sn-3.5Ag solder using Kester 2224-25 aqueous flux at 245°C the maximum wetting force increased steadily from 3.013 mN at 0 percent cold work to 4.298 mN at 50 percent cold work as expected. Conversely, using the Alpha Metals SLS-65 no-clean flux at 245°C the maximum wetting force was -4.886 mN (de-wetting) at 0 percent cold work. The maximum wetting force values became less negative (i.e., transition from de-wetting to wetting) as cold work was increased, such that at 40 percent cold work the maximum wetting force was 2.397 mN. Finally at 50 percent cold work the maximum wetting force was 1.322 mN. Thus, it can be noted that with progressive cold working the maximum

wetting force increased and went from a condition of de-wetting from 0 through 30 percent cold work to a condition of wetting at 40 and 50 percent cold work.

At the higher test temperature of 281°C (T_m + 62°C) the maximum wetting force increased from 0 to 50 percent cold work for both the samples using the aqueous and no-clean fluxes. However, at the higher test temperature the maximum wetting force values were higher than those measured at 245°C. Moreover, de-wetting was not evident with the samples utilizing the no-clean flux. It is theorized that at the higher test temperatures the solder is better able to alloy with the copper substrate, due to the higher thermal excitation of the molten solder alloy and the lower thermodynamic stability of the oxide layer. The results are shown in Figures 15 and 16.

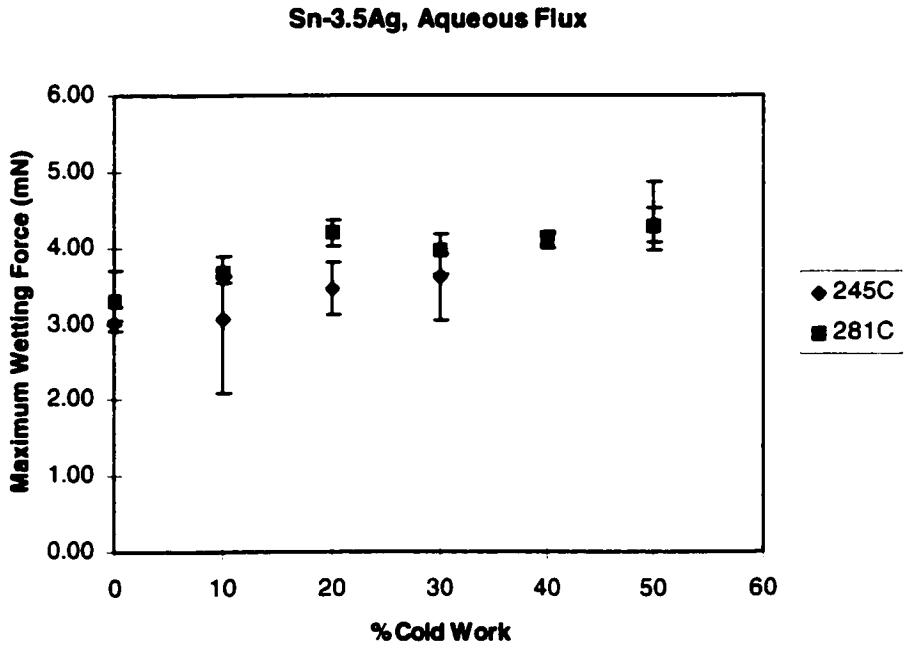

Figure 15: Maximum wetting force as a function of extent of cold work for samples tested using Sn-3.5Ag solder and aqueous flux.

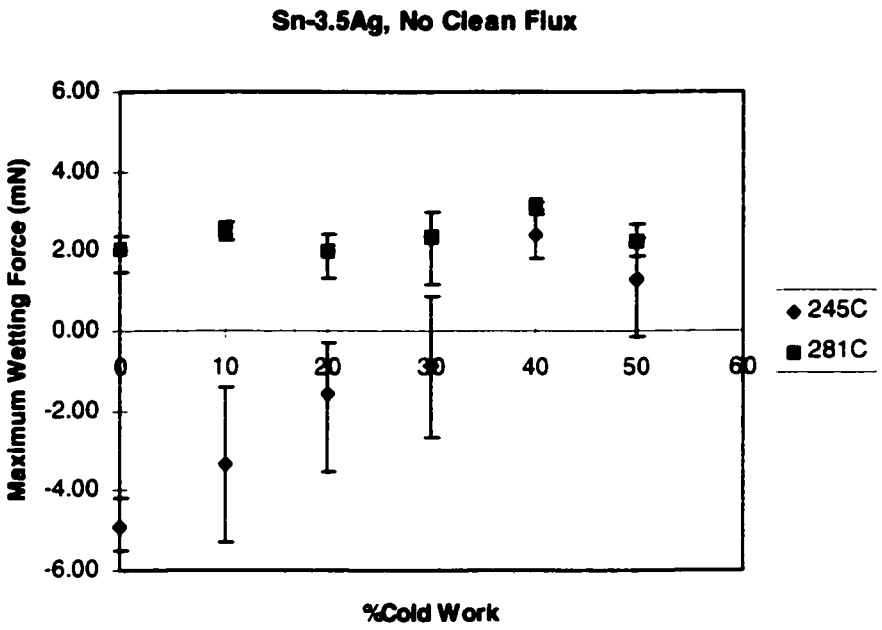

Figure 16: Maximum wetting force as a function of extent of cold work for samples tested using Sn-3.5Ag solder and no-clean flux.

5.1.2 Sn-37Pb

As with the Sn-3.5Ag solder the maximum wetting force for the Sn-37Pb solder at 245°C for both the samples utilizing aqueous and no-clean fluxes increased as the amount of cold work was increased from 0 percent to 50 percent. With the samples using aqueous flux the maximum wetting force increased from 3.722 mN at 0 percent cold work to 4.840 mN at 50 percent cold work. Whereas, with the samples utilizing no-clean flux the maximum wetting force was 3.407 mN at 0 percent cold work and increased to 3.987 mN at 50 percent cold work. Again, similar to the Sn-3.5Ag solder, the maximum wetting force values for the samples using the less aggressive no-clean flux were lower than the samples using the more aggressive aqueous flux. The aqueous flux, because of its more aggressive chemistry, seemed to better remove the oxide from the substrate surface and thus the surface reactions occurred more readily on the samples using the aqueous flux.

Testing was not conducted at the higher temperature of T_m + 62°C since T_m (liquidus temperature) for Sn-37Pb is 189°C and an additional 62°C would essentially be 245°C.

Of particular significance is that the Sn-37Pb samples exhibited the lowest variability of all the solder types tested, as shown in Figures 17 and 18. It is theorized that at the test temperature of 245°C the solder and the copper in the substrate form an alloy layer on the substrate which aids wetting. This is consistent with the findings of Bailey and Watkins that alloying is a necessary condition for wetting and that the extent of wetting is directly related to the amount of metal solubility [18].

5.1.3 Sn-9Zn

Similar to the results for Sn-3.5Ag and Sn-37Pb solders, the maximum wetting force for Sn-9Zn at all flux and temperature combinations tested increased with increasing cold work. In the particular case of Sn-9Zn, utilizing the aqueous flux, at 245°C the maximum wetting force increased from 0.455 mN at 0 percent cold work to 1.826 mN at 50 percent

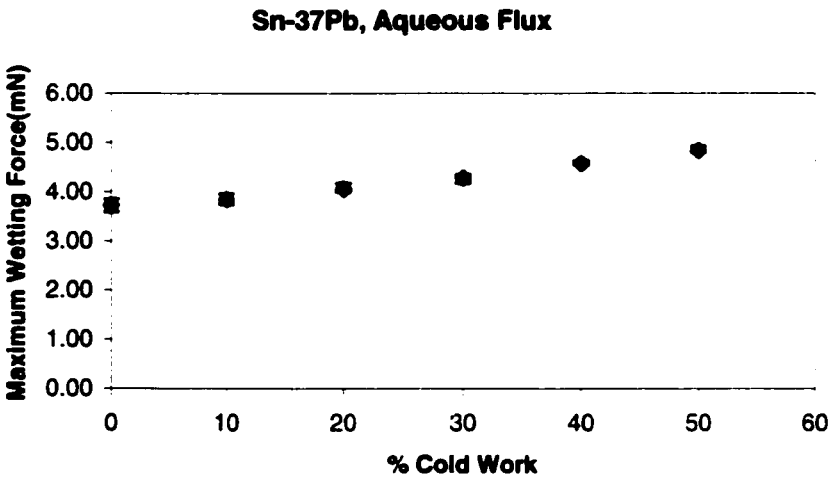

Figure 17: Maximum wetting force as a function of extent of cold work for samples tested using Sn-37Pb solder and aqueous flux.

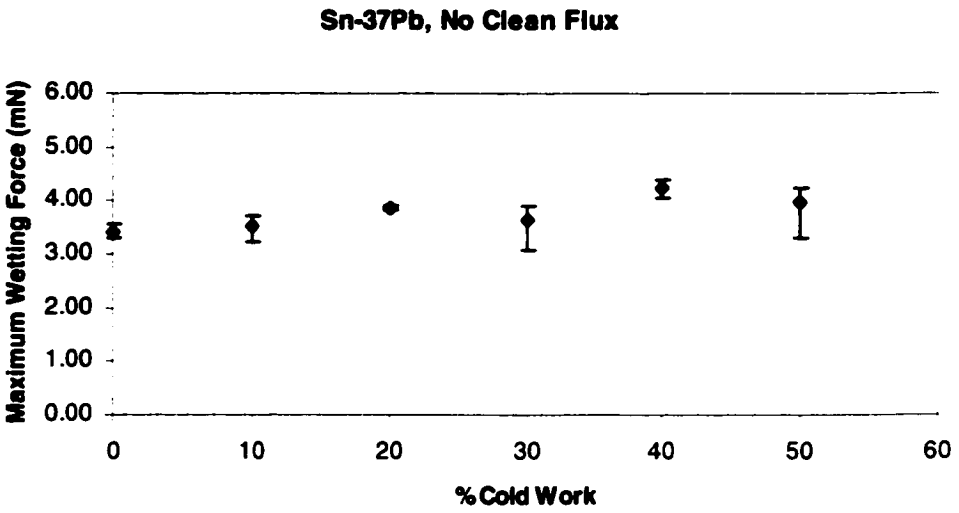

Figure 18: Maximum wetting force as a function of extent of cold work for samples tested using Sn-37Pb solder and no-clean flux.

cold work as shown in Figure 19. When using no-clean flux at 245°C the maximum wetting force was -5.717 mN at 0 percent cold work and progressively increased to -1.198 mN at 50 percent cold work as shown in Figure 20. As with the Sn-3.5Ag and Sn-37Pb solders, the extent of interaction of wetting force was dependent on the type of flux used. The use of the more aggressive aqueous flux resulted in better interaction, as reflected by the positive wetting forces. This is due to the fact that the more aggressive aqueous flux is more effective in removing surface oxidation layers.

At 261°C (T_m+62°C) using aqueous flux the maximum wetting force at 0 percent cold work was 0.728 mN and reached a high of 1.771 mN at 30 percent cold work as shown in Figure 19. At greater than 30 percent cold work the maximum wetting force decreased to 1.746 mN at 40 percent cold work and 1.628 mN at 50 percent cold work. Similarly, at 261°C using the no-clean flux the maximum wetting force was -3.653 mN at 0 percent

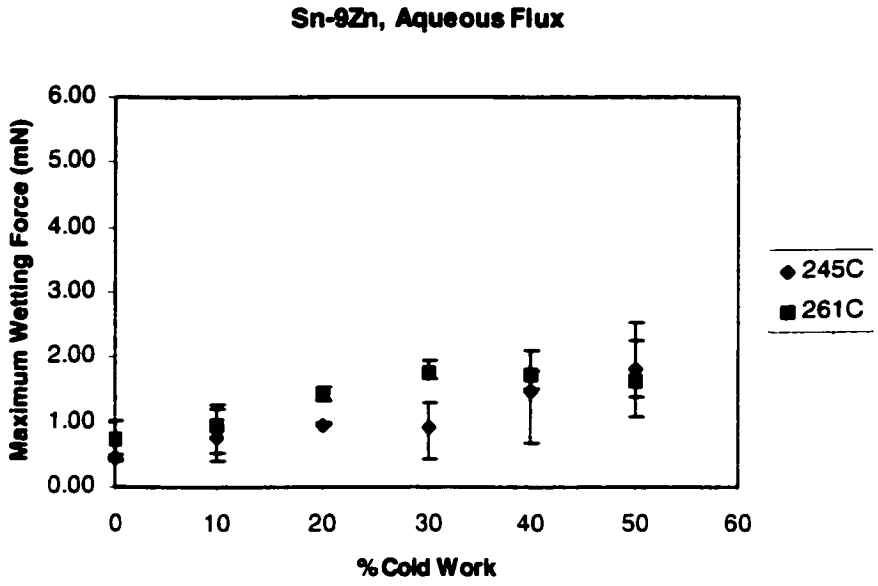

Figure 19: Maximum wetting force as a function of extent of cold work for samples tested using Sn-9Zn solder and aqueous flux.

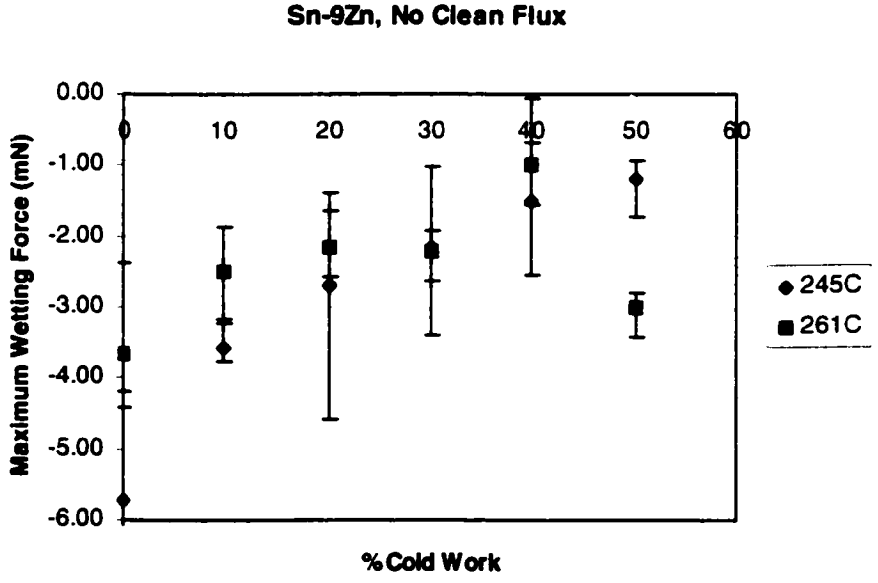

Figure 20: Maximum wetting force as a function of extent of cold work for samples tested using Sn-9Zn solder and no-clean flux.

cold work and then reached a high of -0.990 mN at 40 percent cold work and then decreased to -3.007 mN at 50 percent cold work. This is shown in Figure 20. Again at the higher temperatures there is more thermal excitation for the reactions to occur. Thus, the wetting forces were higher at 261°C as compared to 245°C.

5.1.4 Sn-0.7Cu

The maximum wetting force for the Sn-0.7Cu solder also increased with progressive cold work. At 245°C and using aqueous flux there was a low of 2.846 mN at 0 percent cold work culminating in a high of 3.513 mN at 50 percent cold work. At the same temperature, using no-clean flux, a low of -4.839 mN was measured at 0 percent cold work and a high of -1.948 mN was measured at 20 percent cold work. Beyond 20 percent cold work the maximum wetting force decreased to -2.552 mN, -2.405 mN, and -4.182 mN at 30, 40, and 50 percent cold work respectively (reference Figures 21 and 22).

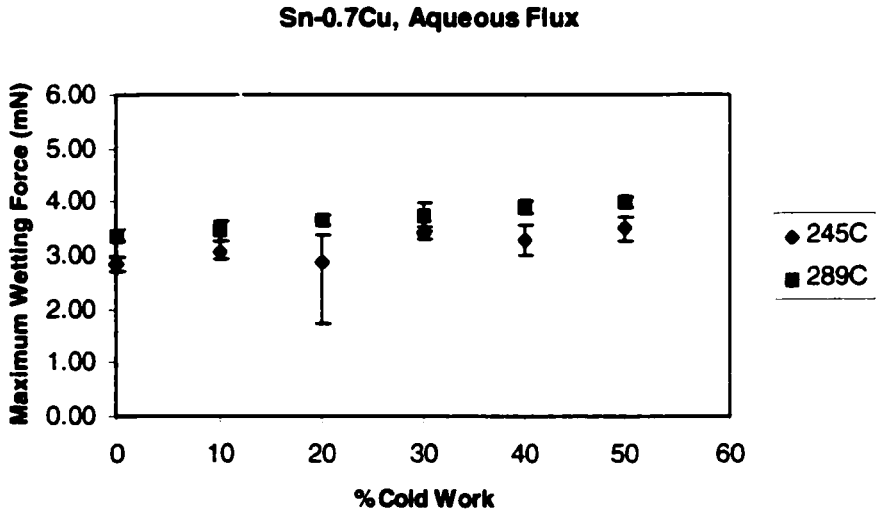

Figure 21: Maximum wetting force as a function of extent of cold work for samples tested using Sn-0.7Cu solder and aqueous flux.

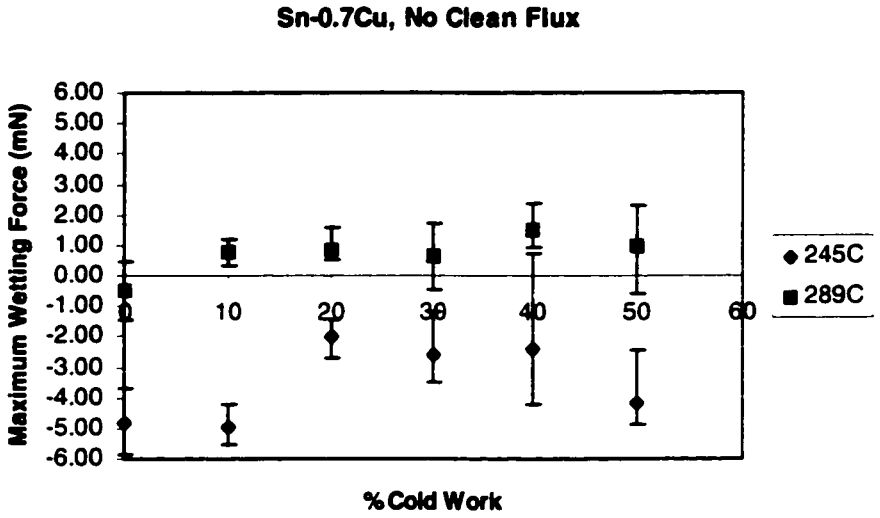

Figure 22: Maximum wetting force as a function of extent of cold work for samples tested using Sn-0.7Cu solder and no-clean flux.

As noted in Section 5.1.1 this tapering off phenomenon with regard to wetting force is noted in the other solders tested and in cold work/corrosion studies. No definitive explanation is known for this phenomenon. Thus, additional work is required. However a possible explanation is that beyond a certain amount of cold working some other factor begins opposing surface free energy and therefore limits the extent of surface reactions such as wetting and/or corrosion.

At the higher test temperature of 289°C, the samples followed a similar pattern to the samples tested at 245°C. For the samples utilizing the aqueous flux at 0 percent cold work the maximum wetting force was 3.364 mN which then progressively increased to a high of 4.013 mN at 50 percent cold work. When the no-clean flux was used at this temperature at 0 percent cold work the maximum wetting force was -0.431 mN which fluctuated at 10, 20, and 30 percent cold work and then reached a high of 1.489 mN at 40 percent cold work. Beyond this point at 50 percent cold work the maximum wetting

force decreased to 1.000 mN. Again this may be the same phenomenon which affected the samples utilizing no-clean flux tested at 245°C and further study is required.

In all samples tested the maximum wetting force increased as the extent of cold work was increased as shown in Tables 2 and 3 and Figures 15 through 22. The increase in maximum wetting force resulted from an increase in the stored energy on the copper coupons during the cold work process. The stored energy or driving force (ΔG) increased the wettability of the solders on the copper coupons. From Tables 2 and 3 and Figures 15 through 22 it can be noted that higher maximum wetting forces were measured when aqueous flux was used rather than no-clean flux. This is expected because the more aggressive aqueous flux is more effective in removing surface oxidation layers and should result in better wetting, as compared to the no-clean flux. In most of the solders tested, except Sn-37Pb at 245°C and Sn-3.5Ag at 281°C, use of the no-clean flux resulted in de-wetting (negative maximum wetting forces). However, the de-wetting condition decreased with increasing cold work, i.e. the values became less negative, and wettability increased in all samples tested using no-clean flux. This is because with higher extent of cold work the surface free energy is higher resulting in better wetting even with the no-clean flux. A further increase in maximum wetting force was noted in all solder/flux combinations when testing was conducted at $T_m + 62°C$. This is because at the higher test temperatures there is more thermal excitation for the reactions to occur.

Overall, the solder with the highest wettability, at all extents of cold work, was Sn-37Pb. The solder with the lowest wettability was Sn-9Zn. The two remaining solders, Sn-3.5Ag, Sn-0.7Cu, had maximum wetting forces between Sn-37Pb and Sn-9Zn. In most cases the increase in maximum wetting force tended to taper off at higher degrees of cold

work (40% and 50%). This tapering off phenomenon was also noted in the author's previous work involving the influence of cold work on corrosion [23]. The reasons for this phenomenon are not known and will be investigated in future work. Also, there tended to be a large variability in the maximum wetting force data as can be noted from Figures 15 though 22 when no-clean flux was used as compared to the aqueous flux. This is because the more aggressive aqueous flux is more effective in removing surface oxidations layers and should results in better wetting, as compared to the no-clean flux. Moreover, data variability decreased further with higher test temperatures because at the elevated temperatures there is more thermal excitation for the reactions to occur.

5.2 Wetting Time

Wetting time is the time required for the wetting curve to cross the corrected zero for buoyancy line. This point is reached when the force acting on the sample is equal to the calculated buoyancy. The results of the wetting time measurements for the specific solders tested are presented in sections 5.2.1 through 5.2.4.

5.2.1 Sn-3.5Ag

With the Sn-3.5Ag solder using Kester 2224-25 aqueous flux at 245°C the time to wetting decreased steadily from 1.10 seconds at 0 percent cold work to 0.19 seconds at 50 percent cold work, as expected. However, using the Alpha Metals SLS-65 no-clean flux at 245°C the time to wetting was more inconsistent and fluctuated from 0.44 seconds at 10 percent cold work to 0.60 seconds at 50 percent cold work. This is shown in Figures 23 and 24. At 0 percent cold work no wetting time was measured because the wetting force data never intersected the corrected zero for buoyancy line, which is the criterion for measurement of wetting time. Between 10 and 50 percent cold work the wetting

increased to 0.77 seconds at 20 percent cold work and increased again to 0.87 seconds at 30 percent cold work. At 40 percent cold work wetting time decreased to 0.36 seconds and then increased to 0.60 seconds at 50 percent cold work. With the aqueous flux, as the extent of cold working was increased the time to wetting decreased. This is not evident with the no-clean flux in which the time to wetting alternately increased or decreased as the extent of cold work increased. The reason for this is that the more aggressive aqueous flux more readily removes surface oxide layers than the no-clean flux. Thus, the time to wetting exhibited a decreasing trend for the samples using the aqueous flux as compared to the no-clean flux in which the time to wetting fluctuated.

At the higher test temperature of 281°C (T_m + 62°C) the time to wetting decreased as the extent of cold work increased from 0 to 50 percent cold work for both the samples using

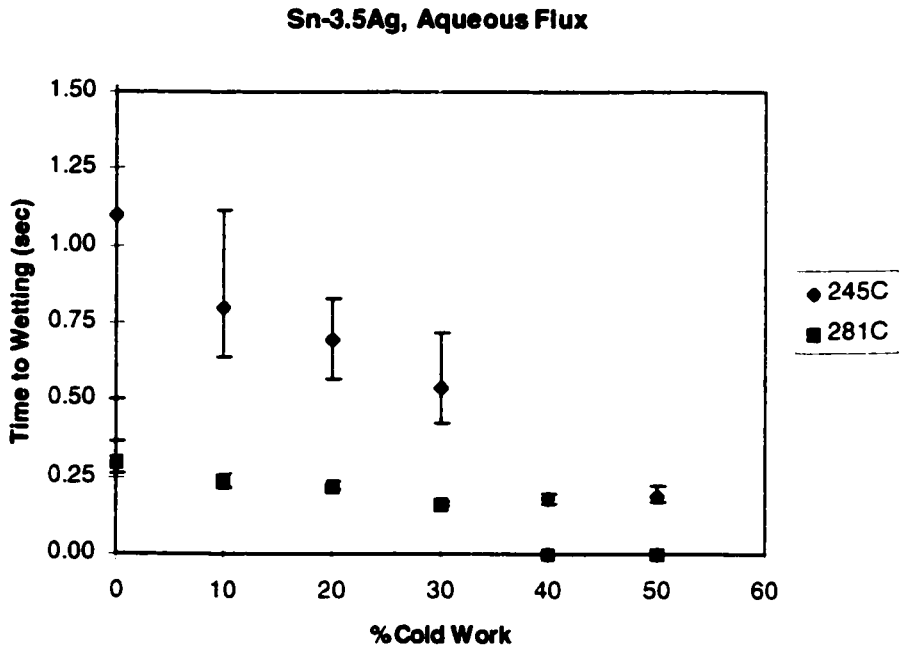

Figure 23: Wetting time as a function of extent of cold work for samples tested using Sn-3.5Ag solder and aqueous flux .

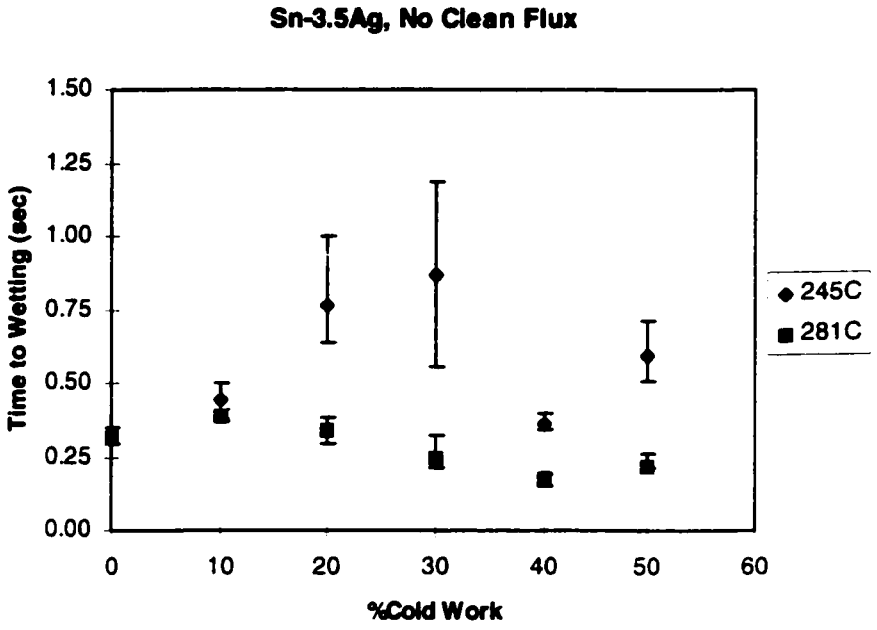

Figure 24: Wetting time as a function of extent of cold work for samples tested using Sn-3.5Ag solder and no-clean flux.

the aqueous and no-clean fluxes. With this higher test temperature there was a smaller range of time to wetting values measured for both the aqueous and no-clean fluxes. As was the case with the wetting force results it is thought that at the higher test temperatures the solder is better able to alloy with the copper substrate, due to the higher thermal excitation of the molten solder alloy and the lower thermodynamic stability of the oxide layer. Thus, regardless of flux used at 281 °C the time to wetting decreased with increasing cold work. This is also shown in Figures 23 and 24.

In all samples tested using the aqueous flux the time to wetting exhibited a linear decreasing trend as the extent of cold work was increased, as shown in Tables V and VI and Figures 23 through 29. The decrease in time to wetting, similar to the increase in maximum wetting force, resulted from an increase in the stored energy on the copper

coupons during the cold work process. The stored energy or driving force (ΔG) decreased the wetting time of the solders on the copper coupons. From Tables V and VI and Figures 23 through 29, it can be noted that those samples utilizing the aqueous flux exhibited a more linear decrease in time to wetting as compared to those samples in which no-clean flux was used. This is expected because the more aggressive aqueous flux is more effective in removing surface oxidation layers and should result in shorter wetting times, as compared to the no-clean flux. A marked decrease in time to wetting was noted in all solder/flux combinations when testing was conducted at $T_m + 62°C$ as compared to 245 °C. This is because at the higher test temperatures there is more thermal excitation for the reactions to occur.

5.2.2 Sn-37Pb

With the Sn-37Pb solder at 245°C utilizing aqueous flux the time to wetting was measured to be 0 seconds for all degrees of cold work tested. The wetting force data for all the samples was above the corrected zero for buoyancy line as data collection began and never intersected the corrected zero for buoyancy line. Therefore, wetting time occurred at essentially 0 seconds because the exact time for wetting to occur was beyond the measurement capabilities of the wetting force balance. The wetting times for the samples tested at 245 °C using the no-clean flux, fluctuated between 0 and 50 percent cold work. A high of 0.30 seconds was measured at 30 percent cold work and a low of 0.20 seconds was measured at 0 percent cold work. The time to wetting for the other extents of cold work fluctuated between these two values and followed no linear decreasing trend. In this respect it is similar to the Sn-3.5Ag samples tested at 245C using the no-clean flux whose wetting time also fluctuated between 0 and 50 percent cold work. This fluctuation is attributable to the less aggressive nature of the no-clean flux.

The aqueous flux, with its more aggressive chemistry, seemed to better remove the oxide from the substrate surface and thus the surface reactions occurred more readily on the samples using the aqueous flux. This is evidenced by the data in Figure 25 where the

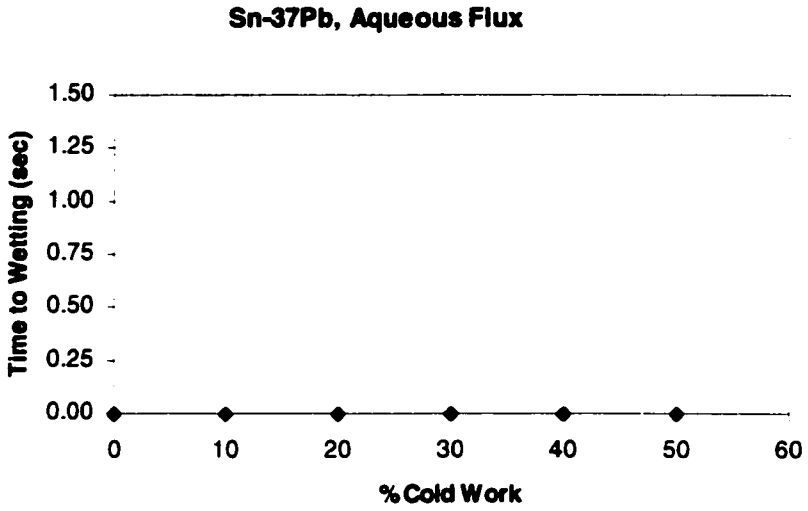

Figure 25: Wetting time as a function of extent of cold work for samples tested using Sn-37Pb solder and aqueous flux.

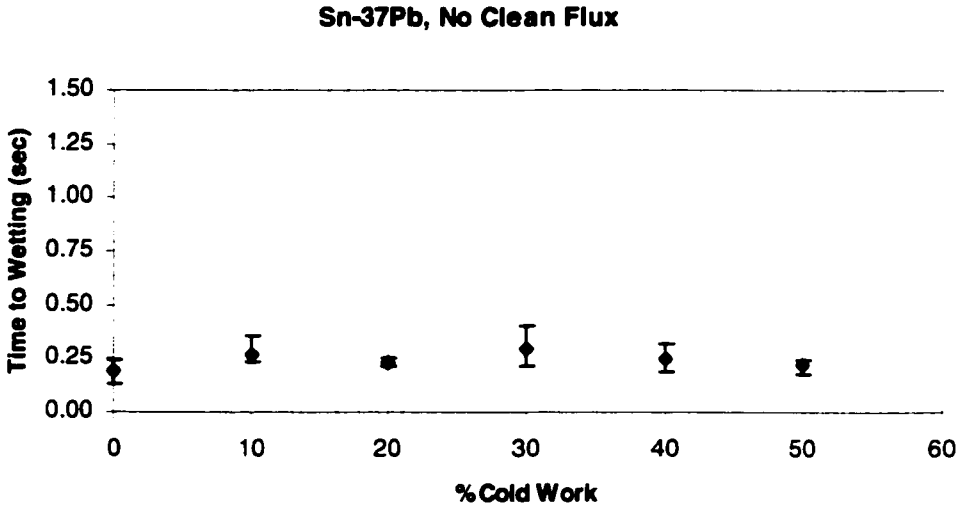

Figure 26: Wetting time as a function of extent of cold work for samples tested using Sn-37Pb solder and no-clean flux.

samples from 0 through 50 percent cold work had time to wetting values of 0 seconds. As noted in Section 5.1.2testing was not conducted at the higher temperature of T_m + 62°C since T_m (liquidus temperature) for Sn-37Pb is 189°C and an additional 62°C would essentially be 245°C. As was the case with the maximum wetting force, the Sn-37Pb samples exhibited the lowest variability of all the solder types utilizing no-clean flux at 245°C tested, as shown in Figure 26. It is theorized that at the test temperature of 245°C the solder and copper from the substrate form an alloy layer on the substrate which aids wetting.

5.2.3 Sn-9Zn

The time to wetting for Sn-9Zn utilizing aqueous flux at 245 °C and T_m + 62 °C decreased linearly with increasing cold work. When using no-clean flux at both 245 °C and 261°C (T_m+62°C) the wetting force data never intersected the corrected zero for buoyancy line which is the necessary criterion for establishing wetting time. Therefore, no time to wetting data were measured for the Sn-9Zn samples using no-clean flux. As with the Sn-3.5Ag and Sn-37Pb solders, the extent of interaction of time to wetting was dependent on the type of flux used. The use of the more aggressive aqueous flux resulted in better interaction, as reflected by the decreasing wetting times. This is due to the fact that the more aggressive aqueous flux is more effective in removing surface oxidation layers.

At 245°C using the aqueous flux the time to wetting decreased linearly from a high of 0.49 seconds at 0 percent cold work to a low of 0.17 seconds at 50 percent cold work. This is shown in Figure 27. Similarly, at 261°C (T_m+62°C) using aqueous flux the time to wetting decreased linearly from a high of 0.32 seconds at 0 percent cold work and a

low of 0.13 seconds at 50 percent cold work as shown in Figure 27. With the higher test temperature of 261°C there was a downward shift in the wetting time as compared to the samples tested at 245 °C. Again at the higher temperatures there is more thermal excitation for the reactions to occur. Thus, the wetting times were shorter at 261°C as compared to 245°C.

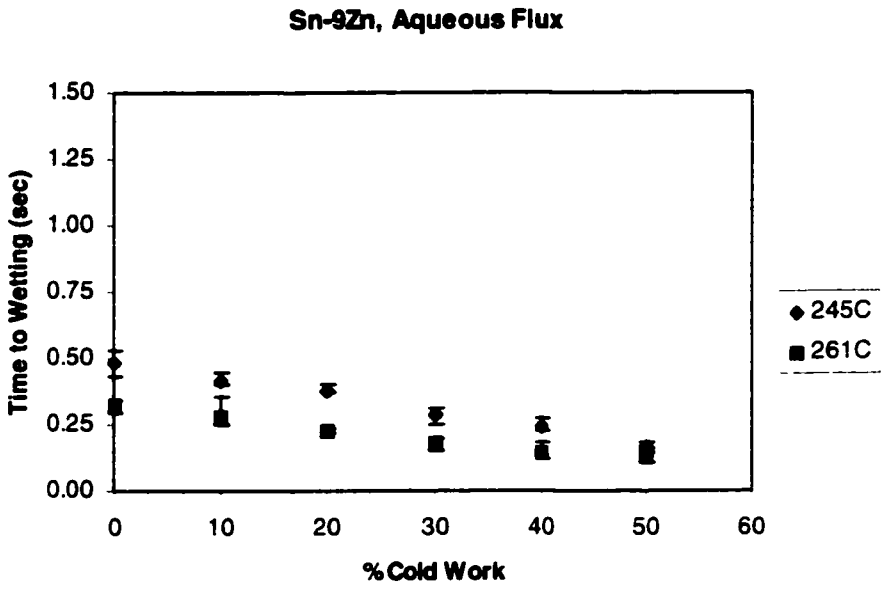

Figure 27: Wetting time as a function of extent of cold work for samples tested using Sn-9Zn solder and aqueous flux.

5.2.4 Sn-0.7Cu

The time to wetting for the Sn-0.7Cu solder using the aqueous flux also decreased with progressive cold work. At 245°C and using aqueous flux there was a high of 1.28 seconds at 0 percent cold work culminating in a low of 0.44 seconds at 50 percent cold work. At 289 °C, using the aqueous flux, there was a high of 0.28 seconds at 0 percent cold work and a low of 0.13 seconds was measured at 50 percent cold work. Conversely, when no-clean flux was used no time to wetting data were measured at 245 °C because

the wetting force data never intersected the corrected zero buoyancy line. At 289 °C, using the no- clean flux, the time to wetting data fluctuated between 0 and 50 percent cold work. A high of 1.08 seconds was measured at 0 percent cold work with a low of 0.38 seconds at 40 percent cold work. Between 0 and 40 percent cold work the time to wetting first decreased at 10 and 20 percent cold work to 0.98 seconds and 0.57 seconds respectively and then increased at 30 percent cold work to 0.75 seconds. Beyond 40 percent cold work the time to wetting increased again to 0.94 seconds (reference Figures 28 and 29).

Overall, the solder with the shortest time to wetting at all extents of cold work was Sn-37Pb. The solder with the longest time to wetting was Sn-0.7Cu. The two remaining solders, Sn-3.5Ag, Sn-9Zn, had time to wetting values between Sn-37Pb and Sn-0.7Cu. There tended to be a large variability in time to wetting data as can be noted from Figures

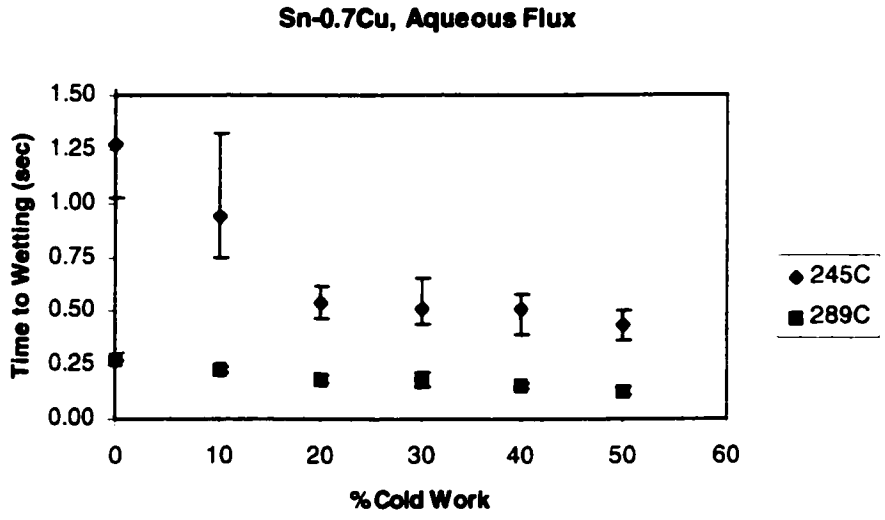

Figure 28: Wetting time as a function of extent of cold work for samples tested using Sn-0.7Cu solder and aqueous flux.

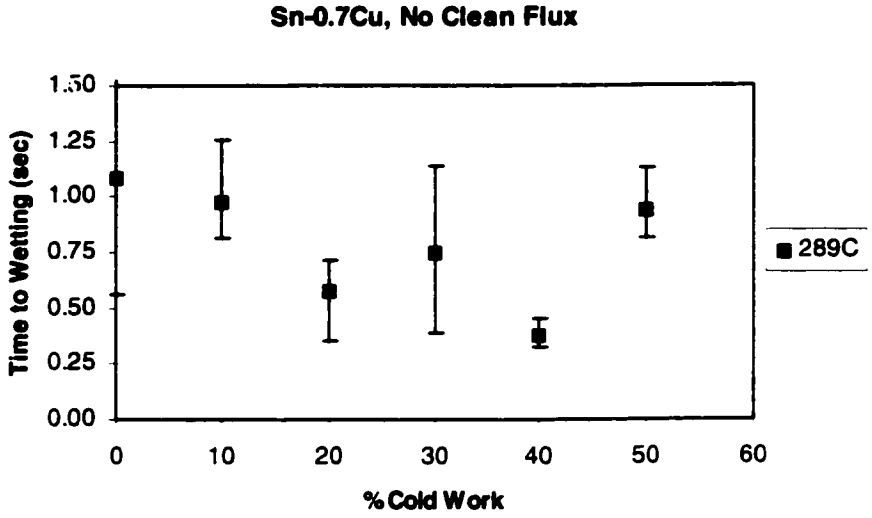

Figure 29: Wetting time as a function of extent of cold work for samples tested using Sn-0.7Cu solder and no-clean flux.

23 though 29 when no-clean flux was used as compared to the aqueous flux. This is because the more aggressive aqueous flux is more effective in removing surface oxidations layers and should result in better wetting, as compared to the no-clean flux. Moreover, data variability decreased further with the higher test temperatures because at the elevated temperatures there is more thermal excitation for the reactions to occur.

5.3 Solder/Surface Interface

Photomicrographs at 1000x magnification of the solder/substrate interface for the 50 percent cold worked samples are shown in Figures 30 through 43. The differences in microstructure between the solders and the copper substrate surface are evident. However, the photomicrographs revealed little of the interaction between the solders and the surfaces of the specimens. Of particular interest would have been the formation of intermetallics at the solder/substrate interface which would confirm alloying between the solders and the substrate and verify wetting. Unfortunately, the test duration of 25

seconds is insufficient for the expected intermetallics to form. Thus, none are evident in the photomicrographs shown in Figures 30 through 43. However, a qualitative comparison between the different solder, flux and temperature combinations can be made. Most notable are the differences in solder layer (blue/grey area in the photomicrographs) thickness between the different solder, flux and temperature samples. A very distinct contrast can be noted between the Sn-37Pb samples, shown in Figure 34 and Figure 35, and the Sn-9Zn solder samples utilizing no-clean flux, shown in Figure 36 and Figure 37. The Sn-37Pb samples have relatively thin solder layer thickness, whereas, the Sn-9Zn samples have wider solder layer thickness with gaps present at the interface between the solder and substrate. If the maximum wetting force data for these samples are reviewed (Tables III and IV) it can be noted that the Sn-37Pb and Sn-9Zn (no-clean flux) represent the two extremes in wetting. The Sn-37Pb samples have the best wetting characteristics of the four solders tested, whereas, the Sn-9Zn (no-clean flux) have the worst wetting characteristics of the solders tested. Therefore, the solder layer thickness seems to be related to the extent of solder wetting.

This phenomenon seems to be most distinct in solder to solder comparisons. However, to a lesser degree it manifests itself when similar solders using different fluxes are compared. Good examples of this phenomenon are the photomicrographs of the Sn-9Zn using aqueous flux (Figures 31 and 33) and Sn-9Zn using no-clean flux (Figures 37 and 39). In Figures 36 and 38 there seems to be good coverage of the solder on the substrate. In Figures 37 and 39 there are noticeable gaps at the solder/substrate interface indicative of poor wetting. Referring back to Tables III and IV these observations are confirmed by the wetting data which shows that the samples in Figures 36 and 38 exhibited better wetting than the samples in Figures 37 and 39.

Although the photomicrographs in Figures 30 through 43 did not reveal the formation of intermetallics they do contain some valuable qualitative information concerning the test samples as noted in the foregoing. Much of this qualitative information is confirmed by the actual wetting data for the samples contained in Tables III and IV. In theory, the formation of intermetallics should have occurred and been evident in the photomicrographs in Figures 30 through 43. However, because of the short test duration of 25 seconds there was insufficient time for the intermetallics to form.

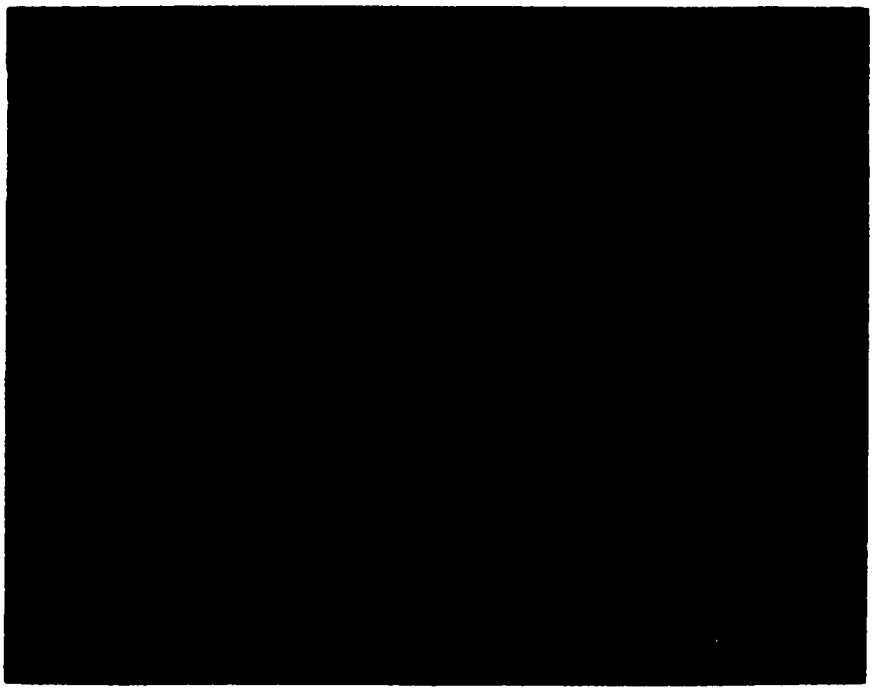

Figure 30: Photomicrograph of Sn-3.5Ag, (aqueous flux, T=245°C), solder substrate interface at 1000x magnification.

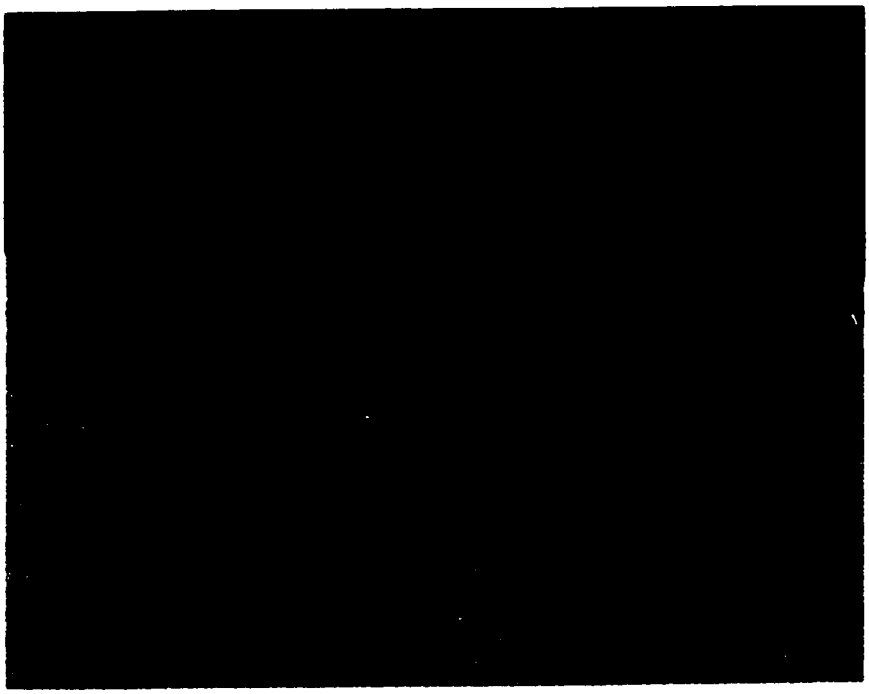

Figure 31: Photomicrograph of Sn-3.5Ag, (no-clean flux, T=245°C), solder substrate interface at 1000x magnification.

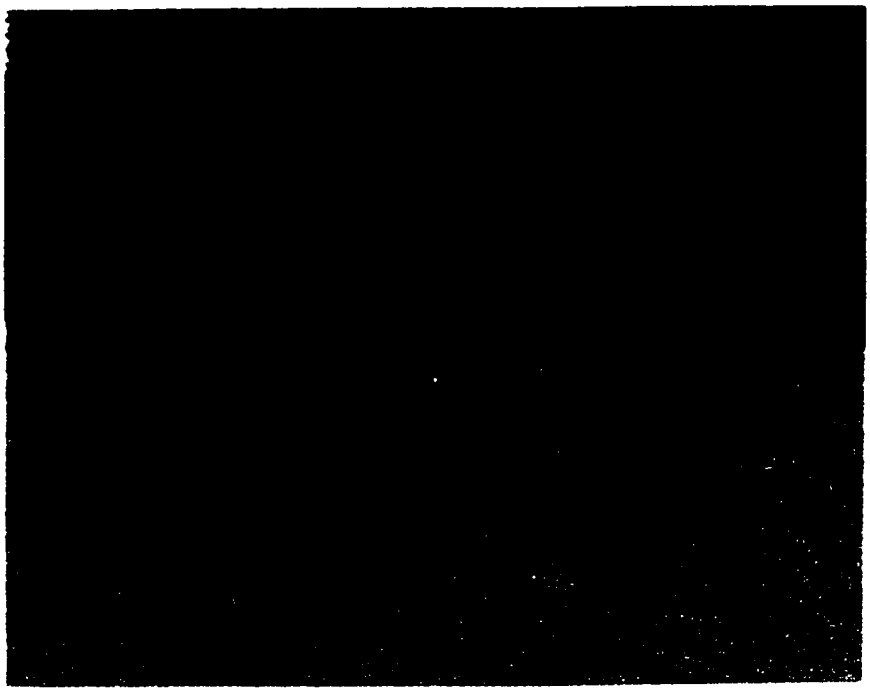

Figure 32: Photomicrograph of Sn-3.5Ag, (aqueous flux, T=281°C), solder substrate interface at 1000x magnification.

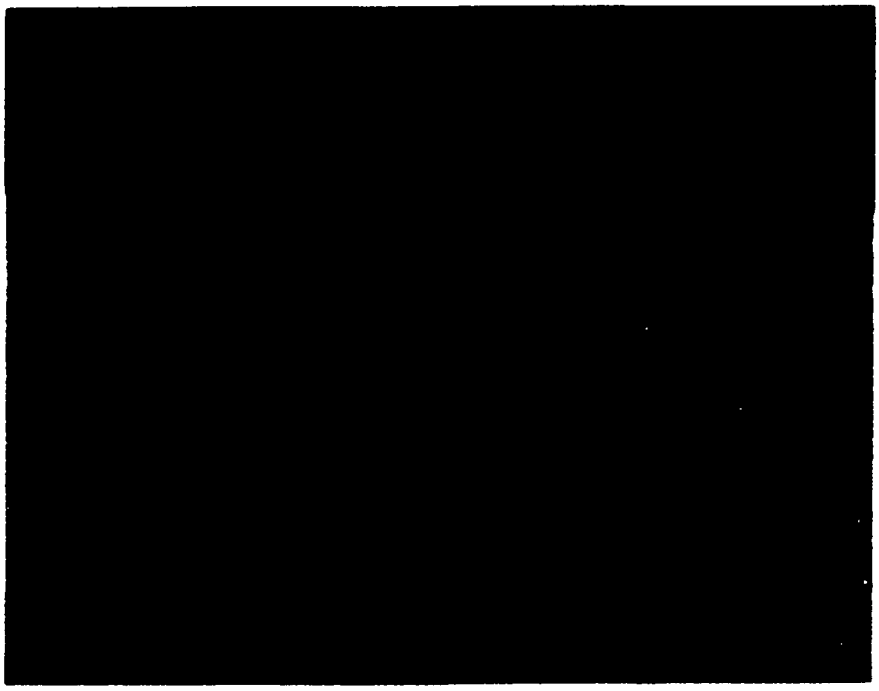

Figure 33: Photomicrograph of Sn-3.5Ag, (no-clean flux, T=281°C), solder substrate interface at 1000x magnification.

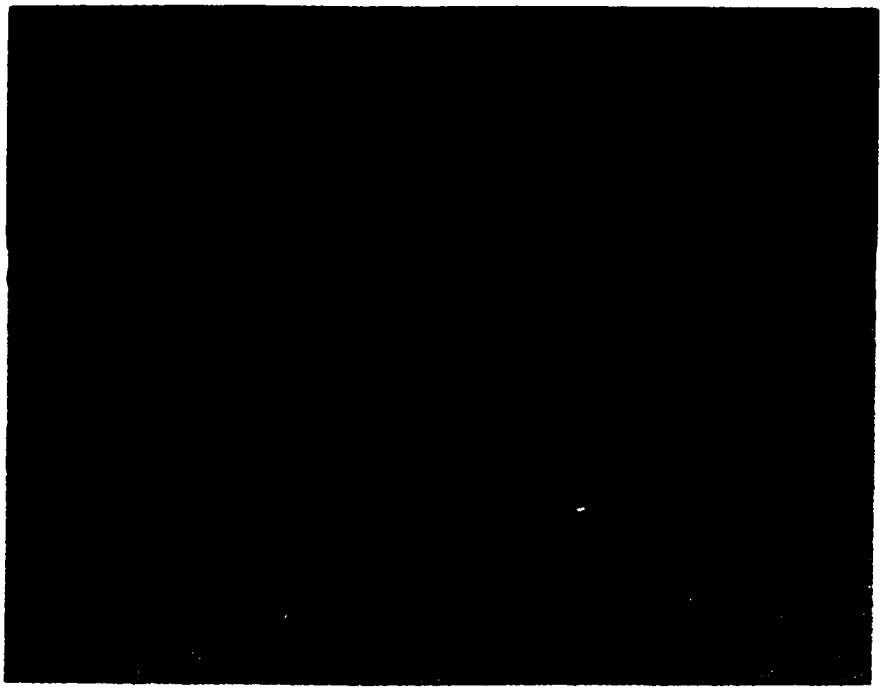

Figure 34: Photomicrograph of Sn-37Pb, (aqueous flux, T=245°C), solder substrate interface at 1000x magnification.

Figure 35: Photomicrograph of Sn-37Pb, (no-clean flux, T=245°C), solder substrate interface at 1000x magnification.

Figure 36: Photomicrograph of Sn-9Zn, (aqueous flux, T=245°C), solder substrate interface at 1000x magnification.

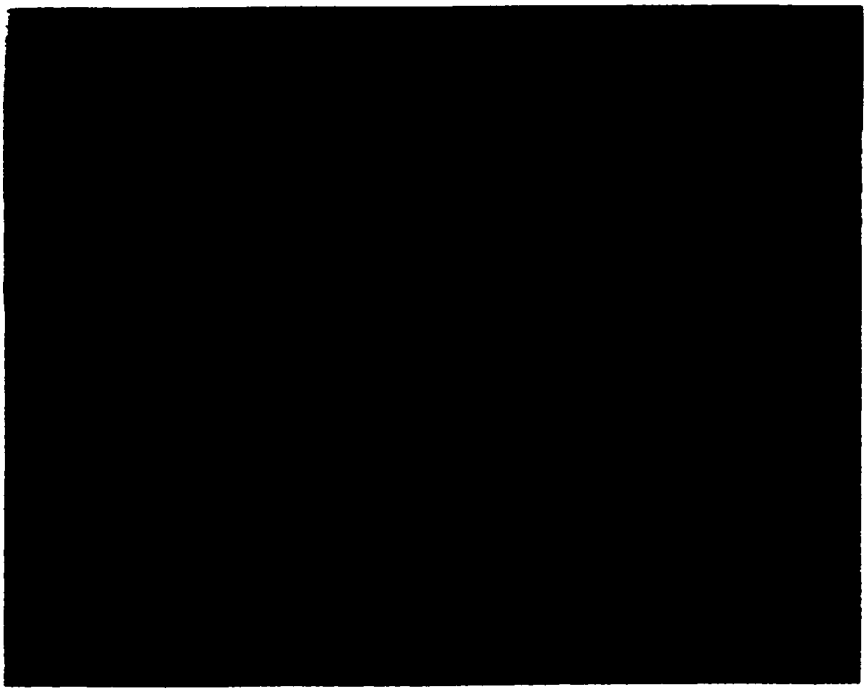

Figure 37: Photomicrograph of Sn-9Zn, (no-clean flux, T=245°C), solder substrate interface at 1000x magnification.

Figure 38: Photomicrograph of Sn-9Zn, (aqueous flux, T=261°C), solder substrate interface at 1000x magnification.

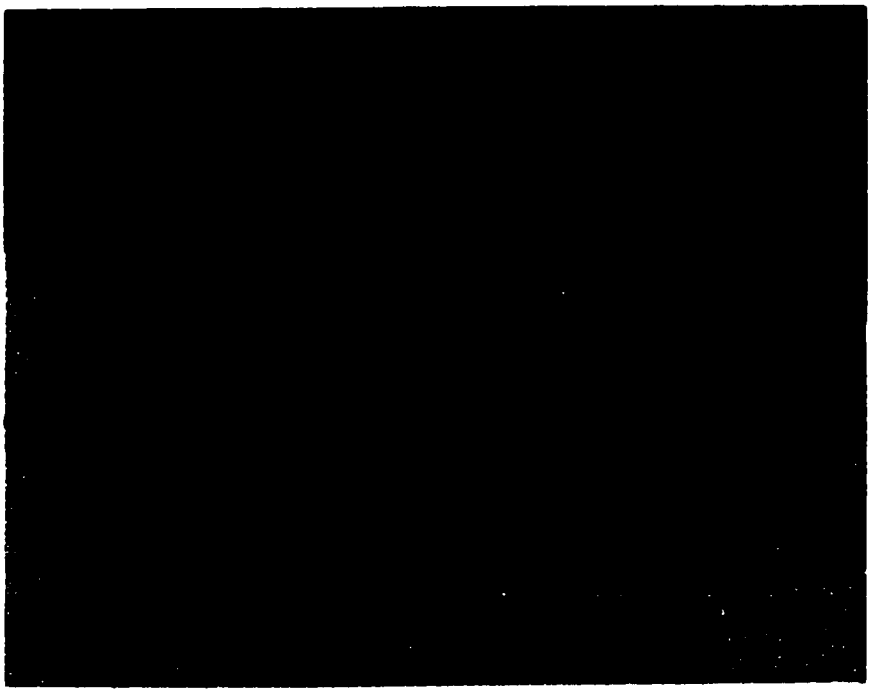

Figure 39: Photomicrograph of Sn-9Zn, (no-clean flux, T=261°C), solder substrate interface at 1000x magnification.

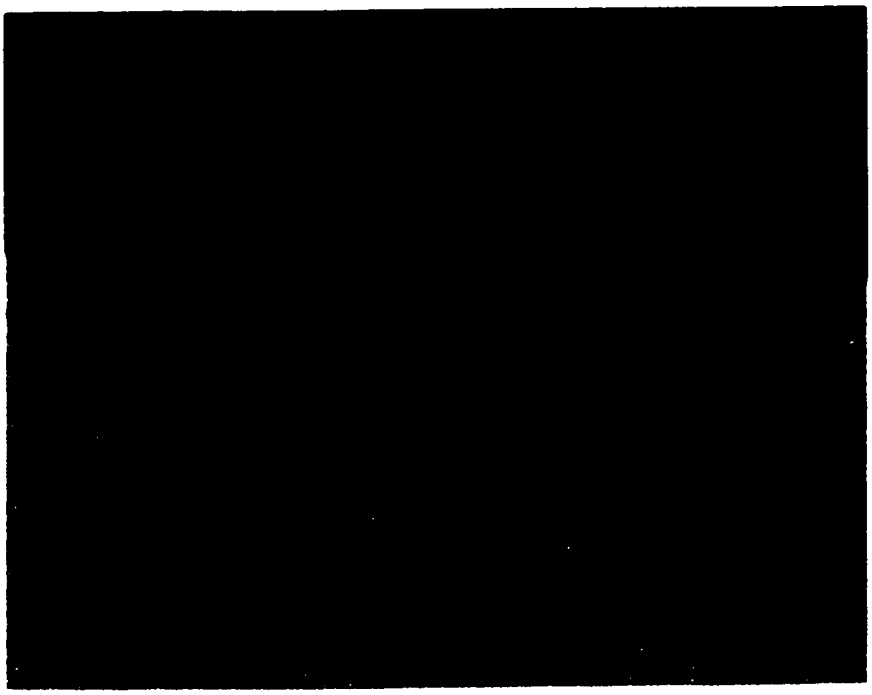

Figure 40: Photomicrograph of Sn-0.7Cu, (aqueous flux, T=245°C), solder substrate interface at 1000x magnification.

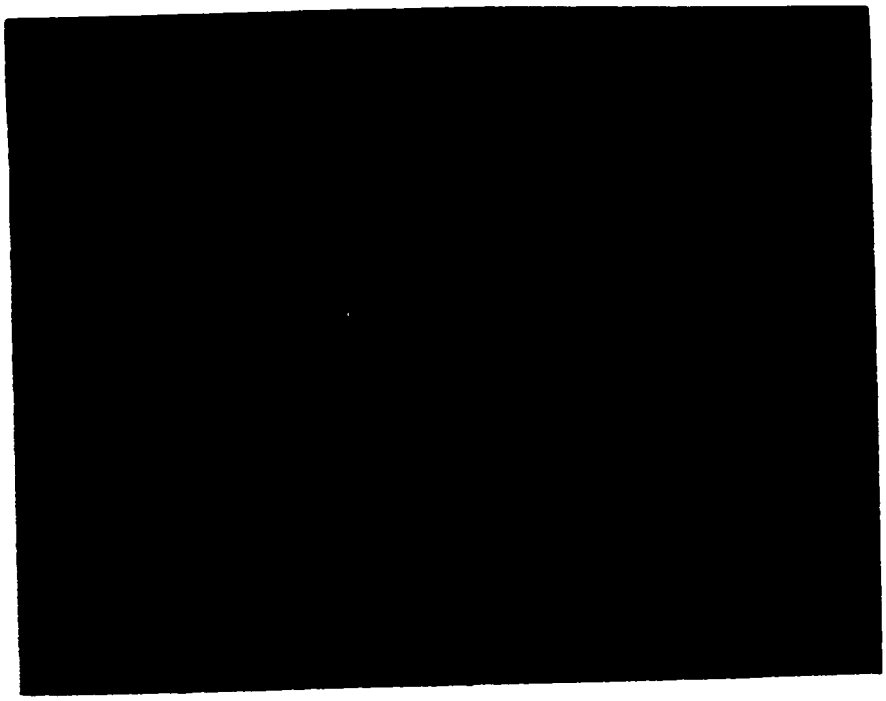

Figure 41: Photomicrograph of Sn-0.7Cu, (no-clean flux, T=245°C), solder substrate interface at 1000x magnification.

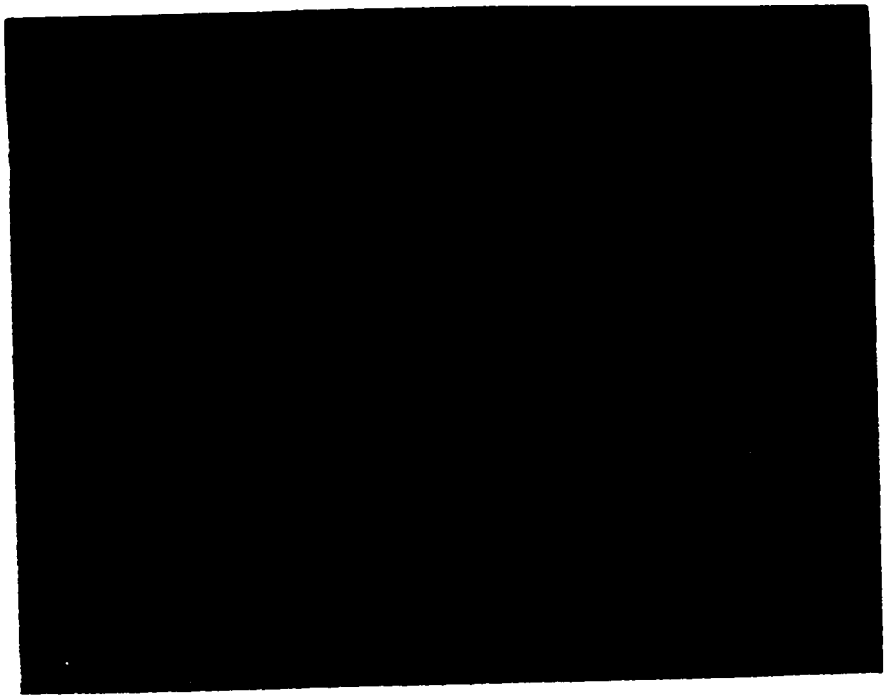

Figure 42: Photomicrograph of Sn-0.7Cu, (aqueous flux, T=289°C), solder substrate interface at 1000x magnification.

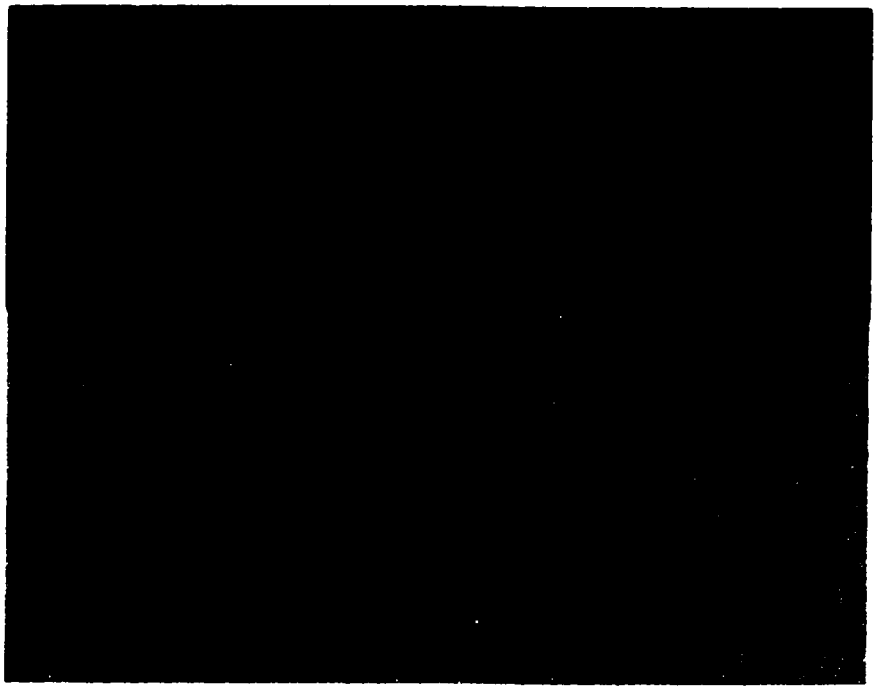

Figure 43: Photomicrograph of Sn-0.7Cu, (no-clean flux, T=289°C),solder substrate interface at 1000x magnification.

CHAPTER SIX
CONCLUSION

The surface condition of a metal influences the ability of a solder to wet that metal. One means of changing the surface condition of a metal is by cold working, which creates dislocations within the metal and puts the metal in a more energetic state. One component of this higher energy state is surface energy which directly influences the ability of a solder to wet a metal. In the case of copper, the primary material of construction for lead frames, cold working can be expected to influence the wetting characteristics of the copper substrate by a solder. The maximum wetting force was found to increase and the wetting time decrease with increased cold work in all samples tested. Of the four solders tested Sn-37Pb (T = 245°C, aqueous flux) exhibited the highest maximum wetting force, shortest time to wetting and therefore best wettability. In general it was found that the maximum wetting force and time to wetting was affected by solder bath temperature and the type of flux used. In particular, the highest maximum wetting forces and shortest wetting times resulted from a combination of high solder bath temperatures (T_m +62°C) and the use of the more aggressive aqueous flux. The higher temperatures and the more aggressive nature of the aqueous flux more thoroughly removed the oxides from the substrate surface, thus improving wettability and time to wet. Samples tested at 245°C with Sn-3.5Ag, Sn-9Zn, and Sn-0.7Cu in combination with the no-clean flux exhibited de-wetting and higher variability between measurements.

Future Work

In terms of future work it would be beneficial to perform the following:

1. X-ray diffraction to quantify the cold work performed on the samples. This will allow better correlation of cold work with wetting force.

2. Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) to provide an elemental makeup of the surface and investigate the existence of intermetallic compounds on the solder/substrate interface

3. Rutherford Backscattering Spectroscopy (RBS) to give a depth profile of the surface structure. When done in combination with AES and XPS this will allow measurement of the thickness of the elemental layers detected by AES and XPS and provide better correlation between extent of cold work, wetting force and extent of alloying.

4. Investigate the reasons for the noted decrease in maximum wetting force beyond 40 percent reduction in thickness. This will provide more insight into what mechanisms operate when a solder wets a metal that has been cold worked and whether a different mechanism dominates beyond 40 percent cold work.

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APPENDIX A
WETTING FORCE DATA

Test Sample Matrix

245C								
	Sn-3.5Ag		Sn-37Pb		Sn-0.7Cu		Sn-9Zn	
%CW	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)
0	1C-5C	1D-5D	1E-5E	1FFF-5FFF	1QQQQ-5QQQQ	1RRRR-5RRRR	1V-5V	1Z-5Z
	1CC-5CC	1F-5F	1EEE-5EEE					
		1VVV-5VVV						
10	1L-5L	1M-5M	1GGG-5GGG	1HHH-5HHH	1MMMM-5MMMM	1NNNN-5NNNN	1X-5X	1EE-5EE
		1M1-5M1						
20	1N-5N	1NN-5NN	1III-5III	1OO-5OO	1WWW-5WWW	1XXX-5XXX	1JJ-5JJ	1KK-5KK
		1P-5P						
		1P1-5P1						
		1P2-5P2						
30	1S-5S	1PP-5PP	1LLL-5LLL	1MMM-5MMM	1AAAA-5AAAA	1BBBB-5BBBB	1JJJ-5JJJ	1KKK-5KKK
		1T-5T						
		1T1-5T1						
40	1SS-5SS	1TT-5TT	1NNN-5NNN	1OOO-5OOO	1EEEE-5EEEE	1FFFF-5FFFF	1WW-5WW	1XX-5XX
50	1CCC-5CCC	1DDD-5DDD	1UUU-5UUU	1IIII-5IIII	1JJJJ-5JJJJ	1AAA-5AAA	1BBB-5BBB	

Tm + 62C								
	Sn-3.5Ag		Sn-37Pb		Sn-0.7Cu		Sn-9Zn	
%CW	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)	Kester 2224-25 (Aqueous)	Alpha Metals Lonco SLS-65 (No-clean)
0	1H-5H	1G-5G	N/A	N/A	1SSSS-5SSSS	1TTTT-5TTTT	1W-5W	1DD-5DD
		1G1-5G1	N/A	N/A				
10	1J-5J	1K-5K	N/A	N/A	1OOOO-5OOOO	1PPPP-5PPPP	1Y-5Y	1FF-5FF
20	1Q-5Q	1R-5R	N/A	N/A	1YYY-5YYY		1LL-5LL	1MM-5MM
		1R1-5R1	N/A	N/A				
30	1RR-5RR	1QQ-5QQ	N/A	N/A	1CCCC-5CCCC	1DDDD-5DDDD	1HH-5HH	1II-5II
			N/A	N/A				
40	1UU-5UU	1VV-5VV	N/A	N/A	1GGGG-5GGGG	1HHHH-5HHHH	1YY-5YY	1ZZ-5ZZ
50	1RRR-5RRR	1SSS-5SSS	N/A	N/A	1KKKK-5KKKK	1LLLL-5LLLL	1PPP-5PPP	1QQQ-5QQQ

Samples 1C-5C

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1C	0.9	3.7	0.7
2C	2	0.9	0.8
3C	1.25	5.5	0.7
4C	2.25	7.7	0.3
5C	1.15	8.6	0.5
Average	1.51	5.28	0.6
Std. Dev.	0.58	3.11	0.2
Minimum	0.900	0.900	0.300
Maximum	2.250	8.600	0.800
-	0.61	4.38	0.30
+	0.74	3.32	0.20

Samples 1CC-5CC

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1CC	0.50	2.91	0.2
2CC	2.25	3.22	0.2
3CC	0.80	2.93	0.2
4CC	0.95	2.90	0.3
5CC	1.00	3.08	0.2
Average	1.10	3.01	0.2
Std. Dev.	0.67	0.14	0.045
Minimum	0.500	2.90	0.200
Maximum	2.250	3.22	0.300
-	0.60	0.1	0.02
+	1.15	0.2	0.08

Samples 1L-5L

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1L	1.115	2.099	0.2
2L	0.772	3.050	0.2
3L	0.642	3.158	0.2
4L	0.773	3.354	0.2
5L	0.709	3.609	0.2
Average	0.80	3.054	0.2
Std. Dev.	0.18	0.575	0.000
Minimum	0.642	2.099	0.200
Maximum	1.115	3.609	0.200
-	0.16	0.96	0.00
+	0.31	0.56	0.00

Samples 1N-5N

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1N	0.750	3.128	0.2
	2N	0.823	3.452	0.2
	3N	0.567	3.658	0.2
	4N	0.657	3.246	0.3
	5N	0.685	3.815	0.2
Average		0.70	3.460	0.22
Std. Dev.		0.10	0.283	0.045
Minimum		0.567	3.128	0.200
Maximum		0.823	3.815	0.300
-		0.13	0.33	0.02
+		0.13	0.36	0.08

Samples 1S-5S

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1S	0.426	3.903	0.2
	2S	0.486	3.040	0.2
	3S	0.532	3.550	0.2
	4S	0.528	3.805	0.2
	5S	0.720	3.835	0.2
Average		0.54	3.627	0.2
Std. Dev.		0.11	0.354	0.000
Minimum		0.426	3.040	0.200
Maximum		0.720	3.903	0.200
-		0.11	0.59	0.00
+		0.18	0.28	0.00

Samples 1SS-5SS

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1SS	0.193	3.991	0.2
	2SS	0.182	4.168	0.2
	3SS	-	-	-
	4SS	0.192	4.139	0.2
	5SS	0.166	4.139	0.2
Average		0.18	4.11	0.20
Std. Dev.		0.01	0.08	0.00
Minimum		0.166	3.991	0.200
Maximum		0.193	4.168	0.200
-		0.02	0.12	0.00
+		0.01	0.06	0.00

Samples 1CCC-5CCC

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1CCC	-	4.080	0.2
	2CCC	-	4.531	0.2
	3CCC	0.169	4.335	0.2
	4CCC	0.177	4.276	0.2
	5CCC	0.220	4.266	0.2
Average		0.19	4.30	0.20
Std. Dev.		0.03	0.16	0.00
Minimum		0.169	4.080	0.200
Maximum		0.220	4.531	0.200
-		0.02	0.22	0.00
+		0.03	0.23	0.00

Samples 1D-5D

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1D	2.8	1.236	0.3
	2D	1.2	2.560	0.2
	3D	2.9	0.686	0.2
	4D	3.2	0.971	0.2
	5D	2.5	2.501	0.2
Average		2.50	1.591	0.22
Std. Dev.		0.76	0.880	0.045
Minimum		1.200	0.686	0.200
Maximum		3.150	2.560	0.300
-		1.30	0.90	0.02
+		0.65	0.97	0.08

Samples 1F-5F

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1F	0.650	2.717	0.2
	2F	0.550	1.373	0.2
	3F	0.700	2.089	0.2
	4F	0.375	3.119	0.2
	5F	0.375	3.011	0.2
Average		0.53	2.462	0.2
Std. Dev.		0.15	0.729	0.000
Minimum		0.375	1.373	0.200
Maximum		0.700	3.119	0.200
-		0.16	1.09	0.00
+		0.17	0.66	0.00

Samples 1VVV-5VVV

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1VVV	-	-5.521	0.2
2VVV	-	-4.207	0.2
3VVV	-	-5.364	0.2
4VVV	-	-4.452	0.3
5VVV	-	-	-
Average	#DIV/0!	-4.89	0.23
Std. Dev.	#DIV/0!	0.65	0.05
Minimum	0.000	-5.521	0.200
Maximum	0.000	-4.207	0.300
-	#DIV/0!	0.64	0.03
+	#DIV/0!	0.68	0.08

Samples 1M-5M

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1M	1.619	0.284	0.2
2M	1.637	0.118	0.3
3M	1.900	0.137	0.3
4M	-	-2.844	0.3
5M	-	-2.717	0.3
Average	1.72	-1.004	0.28
Std. Dev.	0.16	1.623	0.045
Minimum	1.619	-2.844	0.200
Maximum	1.900	0.284	0.300
-	0.10	1.84	0.08
+	0.18	1.29	0.02

Samples 1M1-5M1

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1M1	0.443	1.540	0.2
2M1	0.372	1.422	0.2
3M1	0.432	1.108	0.2
4M1	0.497	0.686	0.2
5M1	0.470	1.265	0.2
Average	0.44	1.204	0.2
Std. Dev.	0.05	0.332	0.000
Minimum	0.372	0.686	0.200
Maximum	0.497	1.540	0.200
-	0.07	0.52	0.00
+	0.05	0.34	0.00

Samples 1NN-5NN

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1NN	-	-	0.3
	2NN	0.292	2.050	0.2
	3NN	0.136	2.766	0.2
	4NN	0.132	2.030	0.2
	5NN	0.492	1.098	0.2
Average		0.26	1.986	0.2
Std. Dev.		0.17	0.684	0.045
Minimum		0.132	1.098	0.200
Maximum		0.492	2.766	0.300
-		0.13	0.89	0.00
+		0.23	0.78	0.10

Samples 1P-5P

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1P	-	-1.952	0.3
	2P	-	-4.148	0.4
	3P	-	-5.306	0.4
	4P	-	-3.844	0.2
	5P	-	-1.402	0.2
Average		#DIV/0!	-3.330	0.3
Std. Dev.		#DIV/0!	1.617	0.100
Minimum		0.000	-5.306	0.200
Maximum		0.000	-1.402	0.400
-		#DIV/0!	1.98	0.10
+		#DIV/0!	1.93	0.10

Samples 1P1-5P1

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1P1	2.800	-0.530	0.3
	2P1	-	-3.177	0.3
	3P1	2.85	-0.726	0.3
	4P1	1.043	1.442	0.3
	5P1	3.100	0.696	0.2
Average		2.45	-0.459	0.2
Std. Dev.		0.95	1.762	0.045
Minimum		1.043	-3.177	0.200
Maximum		3.100	1.442	0.300
-		1.41	2.72	0.00
+		0.65	1.90	0.10

Samples 1P2-5P2

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1P2	-	-	-
	2P2	-	-	-
	3P2	2.85	-0.922	0.2
	4P2	2.40	-0.284	0.3
	5P2	-	-3.531	0.2
Average		2.63	-1.579	0.2
Std. Dev.		0.32	1.720	0.058
Minimum		2.400	-3.531	0.200
Maximum		2.850	-0.284	0.300
-		0.23	1.95	0.00
+		0.23	1.30	0.10

Samples 1PP-5PP

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1PP	1.600	-0.147	0.3
	2PP	1.363	0.029	0.3
	3PP	1.317	-0.108	0.2
	4PP	0.931	0.981	0.2
	5PP	0.859	1.108	0.2
Average		1.21	0.373	0.2
Std. Dev.		0.31	0.618	0.055
Minimum		0.859	-0.147	0.200
Maximum		1.600	1.108	0.300
-		0.36	0.52	0.00
+		0.39	0.74	0.10

Samples 1T-5T

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1T	-	-2.373	0.2
	2T	-	-1.304	0.2
	3T	5.00	-0.706	0.2
	4T	-	-1.373	0.2
	5T	1.514	0.255	0.2
Average		3.26	-1.100	0.2
Std. Dev.		2.46	0.965	0.000
Minimum		1.514	-2.373	0.200
Maximum		5.000	0.255	0.200
-		1.74	1.27	0.00
+		1.74	1.36	0.00

Samples 1T1-5T1

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1T1	0.549	0.843	0.2
2T1	-	-1.216	0.2
3T1	1.19	-0.127	0.2
4T1	-	-2.687	0.4
5T1	-	-1.187	0.3
Average	0.87	-0.875	0.2
Std. Dev.	0.45	1.324	0.089
Minimum	0.549	-2.687	0.200
Maximum	1.186	0.843	0.400
-	0.32	1.81	0.00
+	0.32	1.72	0.20

Samples 1TT-5TT

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1TT	0.341	1.795	0.2
2TT	0.400	2.481	0.2
3TT	0.368	2.403	0.2
4TT	0.368	2.932	0.2
5TT	0.344	2.373	0.2
Average	0.36	2.40	0.20
Std. Dev.	0.02	0.41	0.00
Minimum	0.341	1.795	0.200
Maximum	0.400	2.932	0.200
-	0.02	0.60	0.00
+	0.04	0.54	0.00

Samples 1DDD-5DDD

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1DDD	0.715	-0.167	0.2
2DDD	0.623	0.971	0.2
3DDD	0.556	2.324	0.2
4DDD	0.510	2.010	0.2
5DDD	0.585	1.471	0.2
Average	0.60	1.32	0.20
Std. Dev.	0.08	0.98	0.00
Minimum	0.510	-0.167	0.200
Maximum	0.715	2.324	0.200
-	0.09	1.49	0.00
+	0.12	1.00	0.00

Samples 1E-5E

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1E	0.150	3.638	0.2
	2E	0.150	3.452	0.2
	3E	0.250	3.727	0.2
	4E	0.175	3.511	0.2
	5E	0.175	3.599	0.2
Average		0.18	3.585	0.2
Std. Dev.		0.04	0.108	0.000
Minimum		0.150	3.452	0.200
Maximum		0.250	3.727	0.200
-		0.03	0.13	0.00
+		0.07	0.14	0.00

Samples 1EEE-5EEE

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1EEE	0.127	3.687	0.2
	2EEE	-	-	-
	3EEE	-	3.766	0.2
	4EEE	-	3.589	0.2
	5EEE	-	3.844	0.2
Average		0.13	3.72	0.20
Std. Dev.		#DIV/0!	0.11	0.00
Minimum		0.127	3.589	0.200
Maximum		0.127	3.844	0.200
-		0.00	0.13	0.00
+		0.00	0.12	0.00

Samples 1GGG-5GGG

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1GGG	0.106	3.825	0.2
	2GGG	0.111	3.746	0.2
	3GGG	-	3.952	0.2
	4GGG	0.142	3.805	0.2
	5GGG	-	3.923	0.2
Average		0.12	3.85	0.20
Std. Dev.		0.02	0.09	0.00
Minimum		0.106	3.746	0.200
Maximum		0.142	3.952	0.200
-		0.01	0.10	0.00
+		0.02	0.10	0.00

Samples 1III-5III

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1III		4.040	0.2
2III		4.001	0.2
3III		4.001	0.2
4III		4.090	0.2
5III		4.168	0.2
Average	#DIV/0!	4.06	0.20
Std. Dev.	#DIV/0!	0.07	0.00
Minimum	0.000	4.001	0.200
Maximum	0.000	4.168	0.200
-	#DIV/0!	0.06	0.00
+	#DIV/0!	0.11	0.00

Samples 1LLL-5LLL

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1LLL		4.286	0.2
2LLL		4.178	0.2
3LLL		4.305	0.2
4LLL		4.345	0.2
5LLL		4.325	0.2
Average	#DIV/0!	4.29	0.20
Std. Dev.	#DIV/0!	0.07	0.00
Minimum	0.000	4.178	0.200
Maximum	0.000	4.345	0.200
-	#DIV/0!	0.11	0.00
+	#DIV/0!	0.06	0.00

Samples 1NNN-5NNN

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1NNN	-	-	-
2NNN		4.570	0.2
3NNN		4.550	0.2
4NNN		4.629	0.2
5NNN		4.560	0.2
Average	#DIV/0!	4.58	0.20
Std. Dev.	#DIV/0!	0.04	0.00
Minimum	0.000	4.550	0.200
Maximum	0.000	4.629	0.200
-	#DIV/0!	0.03	0.00
+	#DIV/0!	0.05	0.00

Samples 1UUU-5UUU

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1UUU	0.179	4.246	0.2
	2UUU	0.238	4.197	0.2
	3UUU	0.242	4.040	0.2
	4UUU	0.223	4.158	0.2
	5UUU	0.248	3.295	0.2
Average		0.23	3.99	0.20
Std. Dev.		0.03	0.39	0.00
Minimum		0.179	3.295	0.200
Maximum		0.248	4.246	0.200
-		0.05	0.69	0.00
+		0.02	0.26	0.00

Samples 1FFF-5FFF

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1FFF	0.247	3.501	0.2
	2FFF	0.180	3.315	0.2
	3FFF	0.224	3.325	0.2
	4FFF	0.134	3.560	0.2
	5FFF	0.205	3.334	0.2
Average		0.20	3.41	0.20
Std. Dev.		0.04	0.11	0.00
Minimum		0.134	3.315	0.200
Maximum		0.247	3.560	0.200
-		0.06	0.09	0.00
+		0.05	0.15	0.00

Samples 1HHH-5HHH

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1HHH	0.259	3.550	0.2
	2HHH	0.254	3.609	0.2
	3HHH	0.231	3.727	0.2
	4HHH	0.257	3.432	0.2
	5HHH	0.359	3.217	0.2
Average		0.27	3.51	0.20
Std. Dev.		0.05	0.19	0.00
Minimum		0.231	3.217	0.200
Maximum		0.359	3.727	0.200
-		0.04	0.29	0.00
+		0.09	0.22	0.00

Samples 1OO-5OO

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1OO	0.229	3.864	0.2
	2OO	0.239	3.874	0.2
	3OO	0.216	3.903	0.2
	4OO	0.256	3.825	0.2
	5OO	0.222	3.864	0.2
Average		0.23	3.87	0.20
Std. Dev.		0.02	0.03	0.00
Minimum		0.216	3.825	0.200
Maximum		0.256	3.903	0.200
-		0.02	0.04	0.00
+		0.02	0.04	0.00

Samples 1MMM-5MMM

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1MMM	0.312	3.668	0.2
	2MMM	0.399	3.060	0.2
	3MMM	0.214	3.913	0.2
	4MMM	0.298	3.736	0.2
	5MMM	0.267	3.874	0.2
Average		0.30	3.65	0.20
Std. Dev.		0.07	0.34	0.00
Minimum		0.214	3.060	0.200
Maximum		0.399	3.913	0.200
-		0.08	0.59	0.00
+		0.10	0.26	0.00

Samples 1OOO-5OOO

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1OOO	0.279	4.040	0.2
	2OOO	0.317	4.295	0.2
	3OOO	0.241	4.080	0.2
	4OOO	0.231	4.384	0.2
	5OOO	0.186	4.315	0.2
Average		0.25	4.22	0.20
Std. Dev.		0.05	0.15	0.00
Minimum		0.186	4.040	0.200
Maximum		0.317	4.384	0.200
-		0.06	0.18	0.00
+		0.07	0.16	0.00

Samples 1IIII-5IIII

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1IIII	0.449	3.717	0.2
	2IIII	0.368	3.403	0.2
	3IIII	0.392	3.256	0.2
	4IIII	0.499	3.599	0.2
	5IIII	0.468	3.589	0.2
Average		0.44	3.51	0.20
Std. Dev.		0.05	0.18	0.00
Minimum		0.368	3.256	0.200
Maximum		0.499	3.717	0.200
-		0.07	0.26	0.00
+		0.06	0.20	0.00

Samples 1QQQQ-5QQQQ

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1QQQQ	1.200	2.697	0.4
	2QQQQ	1.028	2.962	0.2
	3QQQQ	1.601	2.766	0.3
	4QQQQ	1.409	2.932	0.3
	5QQQQ	1.165	2.873	0.3
Average		1.28	2.85	0.30
Std. Dev.		0.23	0.11	0.07
Minimum		1.028	2.697	0.200
Maximum		1.601	2.962	0.400
-		0.25	0.15	0.10
+		0.32	0.12	0.10

Samples 1MMMM-5MMMM

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1MMMM	0.742	3.05	0.3
	2MMMM	0.839	3.266	0.3
	3MMMM	1.327	3.079	0.2
	4MMMM	1.000	3.119	0.2
	5MMMM	0.789	2.932	0.3
Average		0.94	3.09	0.26
Std. Dev.		0.24	0.12	0.05
Minimum		0.742	2.932	0.200
Maximum		1.327	3.266	0.300
-		0.20	0.16	0.06
+		0.39	0.18	0.04

Samples 1WWW-5WWW

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1WWW	0.618	1.726	0.2
	2WWW	0.467	2.972	0.2
	3WWW	0.495	3.256	0.2
	4WWW	0.612	3.128	0.2
	5WWW	0.516	3.393	0.2
Average		0.54	2.90	0.20
Std. Dev.		0.07	0.67	0.00
Minimum		0.467	1.726	0.200
Maximum		0.618	3.393	0.200
-		0.07	1.17	0.00
+		0.08	0.50	0.00

Samples 1AAAA-5AAAA

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1AAAA	0.508	3.285	0.2
	2AAAA	0.472	3.354	0.2
	3AAAA	0.649	3.413	0.2
	4AAAA	0.436	3.423	0.2
	5AAAA	0.487	3.531	0.2
Average		0.51	3.40	0.20
Std. Dev.		0.08	0.09	0.00
Minimum		0.436	3.285	0.200
Maximum		0.649	3.531	0.200
-		0.07	0.12	0.00
+		0.14	0.13	0.00

Samples 1EEEE-5EEEE

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1EEEE	0.491	3.227	0.2
	2EEEE	0.393	3.452	0.2
	3EEEE	0.551	3.325	0.2
	4EEEE	0.573	3.560	0.2
	5EEEE	0.572	3.001	0.2
Average		0.52	3.31	0.20
Std. Dev.		0.08	0.22	0.00
Minimum		0.393	3.001	0.200
Maximum		0.573	3.560	0.200
-		0.12	0.31	0.00
+		0.06	0.25	0.00

Samples 1JJJJ-5JJJJ

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1JJJJ		-4.717	0.2
2JJJJ		-4.864	0.4
3JJJJ		-4.433	0.3
4JJJJ		-2.413	0.4
5JJJJ		-4.482	0.4
Average	#DIV/0!	-4.18	0.34
Std. Dev.	#DIV/0!	1.00	0.09
Minimum	0.000	-4.864	0.200
Maximum	0.000	-2.413	0.400
-	#DIV/0!	0.68	0.14
+	#DIV/0!	1.77	0.06

Samples 1RRRR-5RRRR

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1RRRR		-4.825	0.3
2RRRR		-3.707	0.4
3RRRR		-4.345	0.3
4RRRR		-5.845	0.2
5RRRR		-5.472	0.3
Average	#DIV/0!	-4.84	0.30
Std. Dev.	#DIV/0!	0.86	0.07
Minimum	0.000	-5.845	0.200
Maximum	0.000	-3.707	0.400
-	#DIV/0!	1.01	0.10
+	#DIV/0!	1.13	0.10

Samples 1NNNN-5NNNN

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1NNNN		-5.1	0.3
2NNNN		-5.139	0.3
3NNNN		-4.227	0.4
4NNNN		-4.717	0.3
5NNNN		-5.570	0.3
Average	#DIV/0!	-4.95	0.32
Std. Dev.	#DIV/0!	0.50	0.04
Minimum	0.000	-5.570	0.300
Maximum	0.000	-4.227	0.400
-	#DIV/0!	0.62	0.02
+	#DIV/0!	0.72	0.08

Samples 1XXX-5XXX

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1XXX		-2.52	0.2
2XXX		-2.707	0.4
3XXX		-1.432	0.3
4XXX		-1.599	0.4
5XXX		-1.481	0.3
Average	#DIV/0!	-1.95	0.32
Std. Dev.	#DIV/0!	0.61	0.08
Minimum	0.000	-2.707	0.200
Maximum	0.000	-1.432	0.400
-	#DIV/0!	0.76	0.12
+	#DIV/0!	0.52	0.08

Samples 1BBBB-5BBBB

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1BBBB		-3.462	0.3
2BBBB		-3.070	0.3
3BBBB		-2.824	0.3
4BBBB		-1.177	0.3
5BBBB		-2.226	0.3
Average	#DIV/0!	-2.55	0.30
Std. Dev.	#DIV/0!	0.89	0.00
Minimum	0.000	-3.462	0.300
Maximum	0.000	-1.177	0.300
-	#DIV/0!	0.91	0.00
+	#DIV/0!	1.37	0.00

Samples 1FFFF-5FFFF

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1FFFF		-3.403	0.2
2FFFF	2.154	0.736	0.2
3FFFF		-2.050	0.2
4FFFF		-3.070	0.2
5FFFF		-4.237	0.2
Average	2.15	-2.40	0.20
Std. Dev.	#DIV/0!	1.92	0.00
Minimum	2.154	-4.237	0.200
Maximum	2.154	0.736	0.200
-	0.00	1.83	0.00
+	0.00	3.14	0.00

Samples 1AAA-5AAA

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1AAA	0.141	1.500	0.2
	2AAA	0.169	1.383	0.2
	3AAA	0.179	1.785	0.2
	4AAA	0.165	2.256	0.2
	5AAA	0.174	2.207	0.2
Average		0.17	1.83	0.20
Std. Dev.		0.01	0.40	0.00
Minimum		0.141	1.383	0.200
Maximum		0.179	2.256	0.200
-		0.02	0.44	0.00
+		0.01	0.43	0.00

Samples 1V-5V

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1V	0.490	0.471	0.2
	2V	0.467	0.461	0.2
	3V	0.432	0.412	0.2
	4V	0.530	0.510	0.2
	5V	0.510	0.422	0.2
Average		0.49	0.455	0.2
Std. Dev.		0.04	0.040	0.000
Minimum		0.432	0.412	0.200
Maximum		0.530	0.510	0.200
-		0.05	0.04	0.00
+		0.04	0.05	0.00

Samples 1X-5X

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1X			
	2X	0.445	1.255	0.2
	3X	0.398	0.520	0.2
	4X	0.399	0.696	0.2
	5X	0.427	0.657	0.2
Average		0.42	0.782	0.2
Std. Dev.		0.02	0.324	0.000
Minimum		0.398	0.520	0.200
Maximum		0.445	1.255	0.200
-		0.02	0.26	0.00
+		0.03	0.47	0.00

Samples 1JJ-5JJ

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1JJ	-	-	-
2JJ	0.398	0.981	0.2
3JJ	0.367	0.981	0.2
4JJ	0.364	0.951	0.2
5JJ	-	-	-
Average	0.376	0.971	0.200
Std. Dev.	0.02	0.02	0.00
Minimum	0.364	0.951	0.200
Maximum	0.398	0.981	0.200
-	0.01	0.02	0.00
+	0.02	0.01	0.00

Samples 1JJJ-5JJJ

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1JJJ	0.308	0.422	0.2
2JJJ	0.296	1.098	0.2
3JJJ	0.291	1.304	0.2
4JJJ	0.250	0.991	0.2
5JJJ	0.309	0.834	0.2
Average	0.29	0.93	0.20
Std. Dev.	0.02	0.33	0.00
Minimum	0.250	0.422	0.200
Maximum	0.309	1.304	0.200
-	0.04	0.51	0.00
+	0.02	0.37	0.00

Samples 1WW-5WW

Sample	Wetting Time	Maximum Wetting Force	Induction Time
1WW	0.247	0.667	0.2
2WW		1.795	0.2
3WW	0.224	1.638	0.2
4WW	0.231	1.804	0.2
5WW	0.271	1.510	0.2
Average	0.24	1.48	0.20
Std. Dev.	0.02	0.47	0.00
Minimum	0.224	0.667	0.200
Maximum	0.271	1.804	0.200
-	0.02	0.82	0.00
+	0.03	0.32	0.00

Samples 1BBB-5BBB

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1BBB	-	-0.951	0.2
	2BBB	-	-0.922	0.2
	3BBB	-	-1.383	0.2
	4BBB	-	-1.736	0.2
	5BBB	-	-1.000	0.2
Average		#DIV/0!	-1.20	0.20
Std. Dev.		#DIV/0!	0.35	0.00
Minimum		0.000	-1.736	0.200
Maximum		0.000	-0.922	0.200
-		#DIV/0!	0.54	0.00
+		#DIV/0!	0.28	0.00

Samples 1Z-5Z

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1Z	-	-6.708	0.3
	2Z	-	-	-
	3Z	-	-5.874	0.3
	4Z	-	-4.197	0.3
	5Z	-	-6.090	0.3
Average		#DIV/0!	-5.717	0.2
Std. Dev.		#DIV/0!	1.073	0.000
Minimum		0.000	-6.708	0.300
Maximum		0.000	-4.197	0.300
-		#DIV/0!	0.99	-0.10
+		#DIV/0!	1.52	0.10

Samples 1EE-5EE

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1EE	-	-	-
	2EE	-	-3.766	0.2
	3EE	-	-3.168	0.2
	4EE	-	-3.658	0.2
	5EE	-	-3.619	0.2
Average		#DIV/0!	-3.553	0.2
Std. Dev.		#DIV/0!	0.264	0.000
Minimum		0.000	-3.766	0.200
Maximum		0.000	-3.168	0.200
-		#DIV/0!	0.21	0.00
+		#DIV/0!	0.38	0.00

Samples 1KK-5KK

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1KK		-3.030	0.2
	2KK		-2.815	0.2
	3KK		-1.579	0.2
	4KK		-1.383	0.2
	5KK		-4.599	0.2
Average		#DIV/0!	-2.681	0.2
Std. Dev.		#DIV/0!	1.296	0.000
Minimum		0.000	-4.599	0.200
Maximum		0.000	-1.383	0.200
-		#DIV/0!	1.92	0.00
+		#DIV/0!	1.30	0.00

Samples 1KKK-5KKK

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1KKK	-	-	-
	2KKK	-	-2.677	0.2
	3KKK	-	-2.256	0.2
	4KKK	-	-4.609	0.2
	5KKK	-	-3.962	0.2
Average		#DIV/0!	-3.38	0.20
Std. Dev.		#DIV/0!	1.10	0.00
Minimum		0.000	-4.609	0.200
Maximum		0.000	-2.256	0.200
-		#DIV/0!	1.23	0.00
+		#DIV/0!	1.12	0.00

Samples 1XX-5XX

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1XX	-	-2.560	0.2
	2XX	-	-1.863	0.2
	3XX	-	-0.892	0.2
	4XX	-	-1.500	0.2
	5XX	-	-0.686	0.2
Average		#DIV/0!	-1.50	0.20
Std. Dev.		#DIV/0!	0.76	0.00
Minimum		0.000	-2.560	0.200
Maximum		0.000	-0.686	0.200
-		#DIV/0!	1.06	0.00
+		#DIV/0!	0.81	0.00

Samples 1H-5H

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1H	0.363	3.030	0.2
	2H	0.284	3.236	0.2
	3H	0.296	3.119	0.2
	4H	0.256	3.491	0.2
	5H	0.281	3.697	0.2
Average		0.30	3.315	0.2
Std. Dev.		0.04	0.275	0.000
Minimum		0.256	3.030	0.200
Maximum		0.363	3.697	0.200
-		0.04	0.28	0.00
+		0.07	0.38	0.00

Samples 1J-5J

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1J	0.219	3.570	0.2
	2J	0.246	3.893	0.2
	3J	0.220	3.786	0.2
	4J	0.262	3.540	0.2
	5J	0.258	3.570	0.2
Average		0.24	3.672	0.2
Std. Dev.		0.02	0.158	0.000
Minimum		0.219	3.540	0.200
Maximum		0.262	3.893	0.200
-		0.02	0.13	0.00
+		0.02	0.22	0.00

Samples 1Q-5Q

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1Q	0.223	4.031	0.2
	2Q	0.218	4.119	0.2
	3Q	0.207	4.256	0.2
	4Q	0.234	4.266	0.2
	5Q	0.219	4.364	0.2
Average		0.22	4.207	0.2
Std. Dev.		0.01	0.132	0.000
Minimum		0.207	4.031	0.200
Maximum		0.234	4.364	0.200
-		0.01	0.18	0.00
+		0.01	0.16	0.00

Samples 1RR-5RR

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1RR	-	4.011	0.2
	2RR	0.165	3.913	0.2
	3RR	0.152	3.658	0.2
	4RR	0.160	4.188	0.2
	5RR	0.151	4.011	0.2
Average		0.16	3.956	0.2
Std. Dev.		0.01	0.194	0.000
Minimum		0.151	3.658	0.200
Maximum		0.165	4.188	0.200
-		0.01	0.30	0.00
+		0.01	0.23	0.00

Samples 1UU-5UU

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1UU	-	4.050	0.2
	2UU	-	3.991	0.2
	3UU	-	4.011	0.2
	4UU	-	4.197	0.2
	5UU	-	4.207	0.2
Average		#DIV/0!	4.09	0.20
Std. Dev.		#DIV/0!	0.10	0.00
Minimum		0.000	3.991	0.200
Maximum		0.000	4.207	0.200
-		#DIV/0!	0.10	0.00
+		#DIV/0!	0.12	0.00

Samples 1RRR-5RRR

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1RRR	-	4.874	0.2
	2RRR	-	4.070	0.2
	3RRR	-	4.315	0.2
	4RRR	-	4.237	0.2
	5RRR	0.134	3.962	0.2
Average		0.13	4.29	0.20
Std. Dev.		#DIV/0!	0.35	0.00
Minimum		0.134	3.962	0.200
Maximum		0.134	4.874	0.200
-		0.00	0.33	0.00
+		0.00	0.58	0.00

Samples 1G-5G

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1G	-	-2.991	0.3
	2G	1.030	0.461	0.2
	3G	1.555	-0.432	0.2
	4G	0.620	1.461	0.2
	5G	0.546	1.275	0.2
Average		0.94	-0.045	0.2
Std. Dev.		0.46	1.809	0.045
Minimum		0.546	-2.991	0.200
Maximum		1.555	1.461	0.300
-		0.39	2.95	0.00
+		0.62	1.51	0.10

Samples 1G1-5G1

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1G1	0.320	1.451	0.2
	2G1	0.296	2.236	0.2
	3G1	0.306	2.089	0.2
	4G1	0.348	2.118	0.2
	5G1	0.333	2.354	0.2
Average		0.32	2.050	0.2
Std. Dev.		0.02	0.351	0.000
Minimum		0.296	1.451	0.200
Maximum		0.348	2.354	0.200
-		0.02	0.60	0.00
+		0.03	0.30	0.00

Samples 1K-5K

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1K	0.370	2.687	0.2
	2K	-	-	-
	3K	0.375	2.707	0.2
	4K	0.390	2.256	0.2
	5K	0.408	2.373	0.2
Average		0.39	2.506	0.2
Std. Dev.		0.02	0.226	0.000
Minimum		0.370	2.256	0.200
Maximum		0.408	2.707	0.200
-		0.02	0.25	0.00
+		0.02	0.20	0.00

Samples 1R-5R

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1R	0.349	1.030	0.2
	2R	0.352	1.648	0.2
	3R	0.356	1.854	0.2
	4R	0.503	0.530	0.2
	5R	0.342	2.158	0.2
Average		0.38	1.444	0.2
Std. Dev.		0.07	0.657	0.000
Minimum		0.342	0.530	0.200
Maximum		0.503	2.158	0.200
-		0.04	0.91	0.00
+		0.12	0.71	0.00

Samples 1R1-5R1

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1R1	0.385	1.873	0.2
	2R1	0.30	2.403	0.2
	3R1	0.323	2.226	0.2
	4R1	0.352	2.354	0.2
	5R1	0.352	1.324	0.2
Average		0.34	2.036	0.2
Std. Dev.		0.03	0.449	0.000
Minimum		0.300	1.324	0.200
Maximum		0.385	2.403	0.200
-		0.04	0.71	0.00
+		0.04	0.37	0.00

Samples 1QQ-5QQ

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1QQ	0.319	1.147	0.2
	2QQ	0.222	2.668	0.2
	3QQ	0.270	2.197	0.2
	4QQ	0.212	2.981	0.2
	5QQ	0.223	2.913	0.2
Average		0.25	2.381	0.2
Std. Dev.		0.05	0.755	0.000
Minimum		0.212	1.147	0.200
Maximum		0.319	2.981	0.200
-		0.04	1.23	0.00
+		0.07	0.60	0.00

Samples 1VV-5VV

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1VV	0.184	3.050	0.2
	2VV	0.192	3.138	0.2
	3VV	0.153	3.207	0.2
	4VV	0.165	3.207	0.2
	5VV	0.185	3.168	0.2
Average		0.18	3.15	0.20
Std. Dev.		0.02	0.06	0.00
Minimum		0.153	3.050	0.200
Maximum		0.192	3.207	0.200
-		0.02	0.10	0.00
+		0.02	0.05	0.00

Samples 1SSS-5SSS

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1SSS	0.213	2.373	0.2
	2SSS	0.261	2.275	0.2
	3SSS	0.214	1.854	0.2
	4SSS	0.212	2.148	0.2
	5SSS	0.212	2.668	0.2
Average		0.22	2.26	0.20
Std. Dev.		0.02	0.30	0.00
Minimum		0.212	1.854	0.200
Maximum		0.261	2.668	0.200
-		0.01	0.41	0.00
+		0.04	0.40	0.00

Samples 1SSSS-5SSSS

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1SSSS	0.267	3.491	0.2
	2SSSS	0.283	3.246	0.2
	3SSSS	0.276	3.334	0.2
	4SSSS	0.286	3.305	0.2
	5SSSS	0.305	3.442	0.2
Average		0.28	3.36	0.20
Std. Dev.		0.01	0.10	0.00
Minimum		0.267	3.246	0.200
Maximum		0.305	3.491	0.200
-		0.02	0.12	0.00
+		0.02	0.13	0.00

Samples 1OOOO-5OOOO

	Sample	Wetting Time	Maximum Wetting Force		Induction Time
	1OOOO		0.244	3.413	0.2
	2OOOO		0.240	3.246	0.2
	3OOOO		0.232	3.629	0.2
	4OOOO		0.218	3.521	0.2
	5OOOO		0.217	3.580	0.2
Average			0.23	3.48	0.20
Std. Dev.			0.01	0.15	0.00
Minimum			0.217	3.246	0.200
Maximum			0.244	3.629	0.200
-			0.01	0.23	0.00
+			0.01	0.15	0.00

Samples 1YYY-5YYY

	Sample	Wetting Time	Maximum Wetting Force		Induction Time
	1YYY		0.166	3.707	0.2
	2YYY		0.191	3.717	0.2
	3YYY		0.205	3.580	0.2
	4YYY		0.179	3.736	0.2
	5YYY		0.192	3.678	0.2
Average			0.19	3.68	0.20
Std. Dev.			0.01	0.06	0.00
Minimum			0.166	3.580	0.200
Maximum			0.205	3.736	0.200
-			0.02	0.10	0.00
+			0.02	0.05	0.00

Samples 1CCCC-5CCCC

	Sample	Wetting Time	Maximum Wetting Force		Induction Time
	1CCCC		0.210	3.835	0.2
	2CCCC		0.201	3.432	0.2
	3CCCC		0.158	3.972	0.2
	4CCCC		0.163	3.746	0.2
	5CCCC		0.148	3.678	0.2
Average			0.18	3.73	0.20
Std. Dev.			0.03	0.20	0.00
Minimum			0.148	3.432	0.200
Maximum			0.210	3.972	0.200
-			0.03	0.30	0.00
+			0.03	0.24	0.00

Samples 1GGGG-5GGGG

Sample	Wetting Time	Maximum Wetting Force		Induction Time
1GGGG		0.141	4.011	0.2
2GGGG		0.151	3.805	0.2
3GGGG		0.163	3.991	0.2
4GGGG		0.159	4.001	0.2
5GGGG		0.165	3.962	0.2
Average		0.16	3.95	0.20
Std. Dev.		0.01	0.09	0.00
Minimum		0.141	3.805	0.200
Maximum		0.165	4.011	0.200
-		0.01	0.15	0.00
+		0.01	0.06	0.00

Samples 1KKKK-5KKKK

Sample	Wetting Time	Maximum Wetting Force		Induction Time
1KKKK	-		4.021	0.2
2KKKK		0.153	3.982	0.2
3KKKK	-		4.060	0.2
4KKKK	-		4.090	0.2
5KKKK		0.111	3.913	0.2
Average		0.13	4.01	0.20
Std. Dev.		0.03	0.07	0.00
Minimum		0.111	3.913	0.200
Maximum		0.153	4.090	0.200
-		0.02	0.10	0.00
+		0.02	0.08	0.00

Samples 1TTTT-5TTTT

Sample	Wetting Time	Maximum Wetting Force		Induction Time
1TTTT		1.999	-0.765	0.2
2TTTT		0.925	-0.245	0.2
3TTTT		0.845	-0.157	0.2
4TTTT		0.563	0.432	0.2
5TTTT	-		-1.422	0.3
Average		1.08	-0.43	0.22
Std. Dev.		0.63	0.70	0.04
Minimum		0.563	-1.422	0.200
Maximum		1.999	0.432	0.300
-		0.52	0.99	0.02
+		0.92	0.86	0.08

Samples 1PPPP-5PPPP

Sample	Wetting Time	Maximum Wetting Force		Induction Time
1PPPP		1.050	0.314	0.2
2PPPP		0.923	0.726	0.3
3PPPP		1.256	1.177	0.3
4PPPP		0.854	0.657	0.3
5PPPP		0.813	0.941	0.2
Average		0.98	0.76	0.26
Std. Dev.		0.18	0.32	0.05
Minimum		0.813	0.314	0.200
Maximum		1.256	1.177	0.300
-		0.17	0.45	0.06
+		0.28	0.41	0.04

Samples 1DDDD-5DDDD

Sample	Wetting Time	Maximum Wetting Force		Induction Time
1DDDD		0.591	1.157	0.2
2DDDD	-		-	0.2
3DDDD		1.140	-0.461	0.2
4DDDD		0.386	1.687	0.2
5DDDD		0.891	0.186	0.2
Average		0.75	0.64	0.20
Std. Dev.		0.33	0.96	0.00
Minimum		0.386	-0.461	0.200
Maximum		1.140	1.687	0.200
-		0.37	1.10	0.00
+		0.39	1.04	0.00

Samples 1HHHH-5HHHH

Sample	Wetting Time	Maximum Wetting Force		Induction Time
1HHHH		0.336	1.952	0.2
2HHHH		0.450	0.922	0.2
3HHHH		0.369	1.187	0.2
4HHHH		0.329	2.363	0.2
5HHHH		0.402	1.020	0.2
Average		0.38	1.49	0.20
Std. Dev.		0.05	0.63	0.00
Minimum		0.329	0.922	0.200
Maximum		0.450	2.363	0.200
-		0.05	0.57	0.00
+		0.07	0.87	0.00

Samples 1LLLL-5LLLL

	Sample	Wetting Time	Maximum Wetting Force		Induction Time
	1LLLL	0.346		0.873	0.2
	2LLLL	0.328		1.824	0.2
	3LLLL	0.248		2.295	0.2
	4LLLL	-		-	0.2
	5LLLL	0.563		0.598	0.2
Average		0.37		1.40	0.20
Std. Dev.		0.13		0.80	0.00
Minimum		0.248		0.598	0.200
Maximum		0.563		2.295	0.200
-		0.12		0.80	0.00
+		0.19		0.90	0.00

Samples 1W-5W

	Sample	Wetting Time	Maximum Wetting Force		Induction Time
	1W	0.341		1.030	0.2
	2W	0.330		0.520	0.2
	3W	0.293		0.991	0.2
	4W	0.336		0.432	0.2
	5W	0.318		0.667	0.2
Average		0.32		0.728	0.2
Std. Dev.		0.02		0.272	0.000
Minimum		0.293		0.432	0.200
Maximum		0.341		1.030	0.200
-		0.03		0.30	0.00
+		0.02		0.30	0.00

Samples 1Y-5Y

	Sample	Wetting Time	Maximum Wetting Force		Induction Time
	1Y	0.251		1.040	0.2
	2Y	0.352		0.402	0.2
	3Y	0.242		1.138	0.2
	4Y	0.253		1.196	0.2
	5Y	0.278		0.961	0.2
Average		0.28		0.947	0.2
Std. Dev.		0.04		0.318	0.000
Minimum		0.242		0.402	0.200
Maximum		0.352		1.196	0.200
-		0.03		0.55	0.00
+		0.08		0.25	0.00

Samples 1LL-5LL

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1LL	0.240	1.500	0.2
	2LL	0.235	1.412	0.2
	3LL	0.227	1.520	0.2
	4LL	0.238	1.344	0.2
	5LL	0.220	1.559	0.2
Average		0.23	1.467	0.2
Std. Dev.		0.01	0.087	0.000
Minimum		0.220	1.344	0.200
Maximum		0.240	1.559	0.200
-		0.01	0.12	0.00
+		0.01	0.09	0.00

Samples 1HH-5HH

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1HH	0.191	1.785	0.2
	2HH	0.183	1.706	0.2
	3HH	0.153	1.952	0.2
	4HH	0.200	1.667	0.2
	5HH	0.178	1.746	0.2
Average		0.18	1.771	0.2
Std. Dev.		0.02	0.110	0.000
Minimum		0.153	1.667	0.200
Maximum		0.200	1.952	0.200
-		0.03	0.10	0.00
+		0.02	0.18	0.00

Samples 1YY-5YY

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1YY	0.136	1.530	0.2
	2YY	0.162	1.726	0.2
	3YY	0.121	1.785	0.2
	4YY	0.135	2.099	0.2
	5YY	0.180	1.589	0.2
Average		0.15	1.75	0.20
Std. Dev.		0.02	0.22	0.00
Minimum		0.121	1.530	0.200
Maximum		0.180	2.099	0.200
-		0.03	0.22	0.00
+		0.03	0.35	0.00

Samples 1PPP-5PPP

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1PPP	0.136	1.079	0.2
	2PPP	0.136	1.245	0.2
	3PPP	0.162	1.432	0.2
	4PPP	0.123	2.530	0.2
	5PPP	0.108	1.854	0.2
Average		0.13	1.63	0.20
Std. Dev.		0.02	0.58	0.00
Minimum		0.108	1.079	0.200
Maximum		0.162	2.530	0.200
-		0.03	0.55	0.00
+		0.03	0.90	0.00

Samples 1DD-5DD

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1DD	-	-	-
	2DD	-	-3.727	0.2
	3DD	-	-2.383	0.2
	4DD	-	-4.080	0.3
	5DD	-	-4.423	0.3
Average		#DIV/0!	-3.653	0.2
Std. Dev.		#DIV/0!	0.893	0.058
Minimum		0.000	-4.423	0.200
Maximum		0.000	-2.383	0.300
-		#DIV/0!	0.77	0.00
+		#DIV/0!	1.27	0.10

Samples 1FF-5FF

	Sample	Wetting Time	Maximum Wetting Force	Induction Time
	1FF	-	-3.217	0.2
	2FF	-	-2.354	0.2
	3FF	-	-2.442	0.2
	4FF	-	-2.540	0.2
	5FF	-	-1.863	0.2
Average		#DIV/0!	-2.483	0.2
Std. Dev.		#DIV/0!	0.486	0.000
Minimum		0.000	-3.217	0.200
Maximum		0.000	-1.863	0.200
-		#DIV/0!	0.73	0.00
+		#DIV/0!	0.62	0.00

Samples 1MM-5MM

Sample	Wetting Time		Maximum Wetting Force	Induction Time
1MM	-		-2.256	0.2
2MM	-		-1.638	0.2
3MM	-		-2.079	0.2
4MM	-		-2.138	0.2
5MM	-		-2.589	0.2
Average	#DIV/0!		-2.140	0.2
Std. Dev.	#DIV/0!		0.343	0.000
Minimum		0.000	-2.589	0.200
Maximum		0.000	-1.638	0.200
-	#DIV/0!		0.45	0.00
+	#DIV/0!		0.50	0.00

Samples 1II-5II

Sample	Wetting Time		Maximum Wetting Force	Induction Time
1II	-		-2.628	0.2
2II	-		-2.118	0.2
3II	-		-1.971	0.2
4II	-		-2.373	0.2
5II	-		-1.922	0.2
Average	#DIV/0!		-2.202	0.2
Std. Dev.	#DIV/0!		0.296	0.000
Minimum		0.000	-2.628	0.200
Maximum		0.000	-1.922	0.200
-	#DIV/0!		0.43	0.00
+	#DIV/0!		0.28	0.00

Samples 1ZZ-5ZZ

Sample	Wetting Time		Maximum Wetting Force	Induction Time
1ZZ	-		-1.550	0.2
2ZZ	-		-1.285	0.2
3ZZ	-		-1.295	0.2
4ZZ	-		-0.736	0.2
5ZZ	-		-0.059	0.2
Average	#DIV/0!		-0.99	0.20
Std. Dev.	#DIV/0!		0.60	0.00
Minimum		0.000	-1.550	0.200
Maximum		0.000	-0.059	0.200
-	#DIV/0!		0.57	0.00
+	#DIV/0!		0.93	0.00

Samples 1QQQ-5QQQ

Sample	Wetting Time		Maximum Wetting Force	Induction Time
1QQQ			-2.972	0.2
2QQQ			-2.962	0.2
3QQQ			-3.413	0.2
4QQQ			-2.795	0.2
5QQQ			-2.893	0.2
Average	#DIV/0!		-3.01	0.20
Std. Dev.	#DIV/0!		0.24	0.00
Minimum		0.000	-3.413	0.200
Maximum		0.000	-2.795	0.200
-	#DIV/0!		0.41	0.00
+	#DIV/0!		0.21	0.00